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IX. Regnault's *Determination of the Specific Heat of Steam.* *By* J. MACFARLANE GRAY*.

REGNAULT'S experiments on the specific heat of vapours have been interpreted by Regnault as giving results not at all in accordance with the deduction from the kinetic theory of gases, that, for matter travelling in single molecules, the product of the molecular weight by the specific heat is a constant for all substances. I have been led, by considering the order of temperature-pressures for steam, to conclude that the above deduction is true for steam; and I have no doubt, also for all matter travelling in single molecules. When, in 1880, I laid my conclusions before the Physical Society as being corroborated by Regnault's dynamical experiments, it was objected that Regnault's direct thermal experiments gave results widely different from my conclusions; and the report on my paper was that that difference proved that, in the corroborations I had pointed out, I had been led away by merely numerical coincidence.

I will now show that Regnault's thermal experiments have been misinterpreted by Regnault himself, and that he ought to have read the specific heat of steam, according to his experi-

* Read February 25, 1882.

ments, to be exactly in accordance with the deduction of the kinetic theory.

The method of the experiments was to generate steam at 100° C., to superheat it under atmospheric pressure to (say) 125° in one set of experiments, condensing it in a calorimeter to ascertain what quantity of heat was given up, down to 0°. In a second set of experiments with the same apparatus, the temperature was raised to (say) 225°, while the steam was still at atmospheric pressure; this was also condensed in the same calorimeter. It was found that the heat given up by the steam at 225° exceeded that given up by the steam at 125° by 48·051 units of heat; and, dividing by the difference of temperature (100), Regnault found 0·48051 for the specific heat of steam at constant pressure.

In these experiments the superheating to 125° was, no doubt, intended to thoroughly dry the steam, so as to get, in the quantity of heat abandoned in the first set of experiments, the entire heat of complete gasefication, because, if still some moisture remained in the steam, the latent heat of evaporation of that moisture would be included in the difference-quantity supposed to be due to the specific heat of temperature-raising, and, by that amount, the result would be too high.

It appears to me that the completion of the evaporation of suspended moisture cannot be accomplished between 100° and 125°; but it will be more likely to be carried on between 125° and 225°. Particles of liquid remain at the pressure-temperature whatever be the superheated temperature of the gas in which they are suspended. The rate of evaporation of those particles will therefore depend upon the temperature-difference; and in the lower range of temperatures but little of the moisture will be evaporated in its rapid passage through a worm heated to only 25° in excess of the pressure-temperature. In the second set of experiments the excess of temperature was 125°.

To test this, let similar experiments be made at 100°; and if the resulting apparent specific heats between 100° and 125° are higher than those obtained by Regnault between 125° and 225°, then my argument is demolished; but if the results are smaller, then my suspicions have been justified, and a correction is required on the results as given by

Regnault. Fortunately for my object, Regnault has left us (in vol. i., at page 695) the data of thirty-eight reliable experiments on the "total heat" of steam at 100° down to 0°, giving the mean = 636·70 units of heat. I have, with this "total heat" for 100°, compared the results of the experiments on the steam of 125°—in precisely the same way as Regnault worked for the interval between 125° and 225° (these experiments are recorded in vol. ii., pages 167–178). The results of my calculations are given below. The first two series were merely preparatory trials to arrive at the best form of apparatus; and only a few grammes of vapour were passed through the worm at each of those experiments. In the third and the fourth series ten times as much vapour was passed through on each occasion. Regnault says:—"J'ai pu opérer ainsi sur des quantités de vapeur beaucoup plus considérables, et diminuer l'importance relative des corrections produites par les causes perturbatrices." This consideration is still more important when the range of temperature is limited to 25°—only one fourth of the range from which Regnault deduced his result. The large calorimeter was used only in the third and fourth series.

First series.	Second series.	Third series.	Fourth series.
·280	·546	·299	·386
·465	·591	·314	·381
·417	·567	·340	·346
·377		·375	·309
·463	Mean ·567	·400	·427
		·411	·463
Mean ·400		·349	
		·413	Mean ·3853
Preparatory trials.		·405	
		·415	
		Mean ·3721	

That the method of calculation may be perfectly clear, I give the particulars for the first experiment in the fourth series. Superheating to 124°·81, each unit of vapour gave up 646·28 units of heat down to 0°. Steam at 100° gave up 636·70 down to 0°.

$$\frac{646{\cdot}28 - 636{\cdot}70}{124{\cdot}81 - 100} = {\cdot}386.$$

The quantity of vapour in this experiment was 102·62 grms.; the quantity in the first of the first series was only 8·957 grms.

The fourth series was made with an apparatus which was an improvement on that used in the third series; and, taking that series only, adding the probable amount of moisture which would remain at 100° temperature (say 1 per cent. on the ·385), the result is ·389; this, on other grounds, I believe to be nearly correct. If, however, neglecting the other grounds for my opinion, we take the mean of the means of the third and the fourth series, we get

$$\frac{\cdot 3721 + \cdot 3853}{2} = \cdot 3787.$$

This is what Regnault might fairly have done.

If we now calculate what Regnault's experiments would give as the kinetic-theory result, we get the specific heat of hydrogen, at page 121, "mean = 3·4090;" and taking the molecular weight of steam =17·96, we find the specific heat of steam

$$3 \cdot 409 \times \frac{2}{17 \cdot 96} = \cdot 3796.$$

That is to say, the kinetic theory and the thermal determination give almost identically the same number.

This is, I believe, the first experimental proof that the law of "inversely as the molecular weights" applies to compound gases.

X. *The Effect of Temperature on the Electrical Resistance of Mixtures of Sulphur and Carbon.* *By* Shelford Bidwell, *M.A., LL.B.**

Since December 1880 I have from time to time made a number of experiments with the object of ascertaining whether sulphur could, under any circumstances, be made to exhibit the remarkable property possessed by selenium, and in a smaller degree by tellurium, of having its electrical resistance diminished by the action of light.

Amongst other things, the effect was tried of mixing it with

* Read March 25, 1882.

graphite. The sulphur was heated to a temperature a little above its melting-point (115° C.), and when quite liquid a small quantity of tolerably pure powdered plumbago was stirred into it. The liquid mixture was then poured into moulds and allowed to cool quickly. Sticks or plates were thus produced of a substance which in general appearance closely resembled crystalline selenium, its surface being dull and slate-coloured, and its fracture metallic, not unlike that of cast iron.

A short stick of this substance was fitted with platinum electrodes (platinum wires being made red hot and pressed into the two ends), and was joined up in circuit with a Leclanché cell and a reflecting galvanometer. The spot of light was brought to the zero-point at the middle of the scale by means of a magnet, and the sulphur rod exposed to the radiation of a gas-flame which was held within a few inches of it. The spot at once began to move, showing a considerable change in the resistance of the rod. The gas-flame was extinguished; and the spot slowly returned to zero. Upon examination, however, it appeared that the behaviour of this sulphur rod differed from that of crystalline selenium in two important particulars. In the first place, the change of resistance was clearly an effect not of light, but of temperature. Burning magnesium produced no greater change than the gas-flame when held at the same distance. Sunlight was found to have a powerful effect, which was scarcely diminished when the light was caused to pass through red glass; but blue glass or a cell containing water formed an effectual screen. A black hot poker, or even the warmth of the finger, caused a greater deflection than a strong light which was too far removed to heat the rod sensibly.

Now there can be little doubt that the decrease in the resistance of selenium which occurs under the influence of radiation is totally distinct from any effect produced by temperature. It is of course true that absorption of radiations is followed by a rise of temperature, particularly when such radiations belong to the red and infra-red part of the spectrum; but it is not, I think, the fact that such rise of temperature is in any way connected with the remarkable variation of resistance under the influence of light, which, owing to

the invention of the photophone, has lately attracted so much attention. The electrical effects of radiation are, in this case at least, no more due to rise of temperature than are its chemical effects. The evidence in favour of this assertion seems to me to be overwhelming; and I hope to return to it upon another occasion, with special reference to the paper in support of the opposite view read last year by Dr. Moser.

The second point in which the sulphur rod appeared to differ from selenium, was in the *direction* of the change which the radiation of the gas-flame produced, the galvanometer showing that its resistance was increased, instead of being diminished as might have been expected. Here, however, upon the supposition that the effect is due to heating, the behaviour of the sulphur is really similar to that of selenium; for my experiments (agreeing with those of Prof. Adams) show that at ordinary temperatures slight heating is always accompanied by considerably increased resistance.

After numerous trials, in order to ascertain what proportions of sulphur and graphite yielded the greatest sensitiveness to heat, it appeared that a mixture containing 20 parts by weight of sulphur to 9 of graphite was the most suitable. It was also found to be more sensitive when cooled rather quickly than when cooled slowly, though its specific resistance (which is always high) was generally lower in the latter case.

In order that the peculiar property of the substance may be exhibited in the most effective manner, it is necessary to arrange it in thin films, so that a large surface relatively to the bulk may be exposed to the action of radiation. This was at first done by spreading it as thinly and evenly as possible upon plates of mica having tinfoil electrodes at each end. An objection to this method, however, was the enormously high resistance which it involved, amounting sometimes to several hundred thousand ohms. I therefore adopted the device which I generally use in the construction of selenium cells, and which is a simple modification of a plan originally proposed by Dr. Werner Siemens.

Two wires, preferably of platinum, are wound parallel to each other, and very close together, around a slip of mica, care being taken that the wires do not touch each other at

any point. A film of the melted mixture is spread evenly over one surface of the mica; and the wire electrodes are thus connected with each other through half their entire length by a series of very narrow strips of the sulphur mixture.

The resistance of a sulphur "cell" constructed in this manner was 9100 ohms at a temperature of 14° C. The cell was slowly heated in an air-bath, and the resistance measured as accurately as possible at almost every degree. The following table sufficiently indicates the rate at which the resistance increased.

Temperature.	Resistance.
14° C.	9,100 ohms.
19°	11,400 „
25°	13,700 „
30°	16,700 „
35°	20,600 „
40°	26,900 „
45°	34,000 „
50°	42,900 „
55°	57,000 „

Thus at 55° the resistance of the cell was more than six times as great as at 14°.

Upon another occasion the cell was raised to a much higher temperature. No measurements were made with the bridge, however, the cell being simply connected with a battery and a galvanometer, and the deflections noted from time to time. After passing 55°, the resistance increased with great rapidity, until at a temperature of 100° it was sensibly infinite, there being no movement of the spot of light when the circuit was opened with a key. Immediately after passing 100°, the resistance began to fall even more quickly than it had risen. The deflection at 105° was the same as that at 85°; at 110° the same as at 65°; at 114° the same as at 50°; and at 115° the same as at 35°. The spot of light now became so unsteady (probably in consequence of the melting of the cell) that it was not possible to carry the experiment further.

A mixture has also been prepared in which lampblack was used instead of graphite; but very few experiments have yet been made with it, and the results obtained have not been

uniform. At ordinary temperatures it generally behaves like the graphite mixtures; but its temperature of maximum resistance is probably lower than 100°. In one case indeed, in which the proportions were 8 parts of sulphur to 1 of lampblack, the resistance was found to be greatest at 15° (530,000 ohms), any change in the temperature, whether in the direction of heat or cold, producing a decrease. But since no such effect has been produced with other specimens of the same compound, I am inclined to think that it is due to some unnoticed peculiarity in the construction of the cell.

With this single exception, every specimen of the mixtures, whether made with graphite or lampblack, has at ordinary temperatures been found to have its resistance increased by heat.

At first sight this appears to be a very paradoxical phenomenon. It is now generally admitted that the resistance of graphite and other forms of carbon is diminished by heat; and it is also commonly believed that a rise of temperature invariably causes a decrease in the resistance of insulators such as sulphur. The compound of sulphur and carbon with which we have to do is certainly only a mechanical mixture (for no chemical combination could be formed at a temperature of 150° C., which is never exceeded in making the preparation); yet the effect which heat produced upon it is exactly opposite to that produced upon each of its constituents.

Some experiments were made in order to determine the effect of heat upon the resistance of carbon and sulphur separately; but, although in the case of sulphur some unexpected results were obtained, nothing whatever was observed which would *per se* account for the variations of resistance in the sulphur and carbon mixtures.

I believe the true explanation to be this:—The mixture does not consist of a uniform structureless mass of sulphur having particles of carbon imbedded in and completely surrounded by it. It is in fact an aggregation of little crystals of sulphur, with carbon packed between them like mortar between bricks. The conduction thus takes place entirely through the carbon particles, which may be considered as extending in a series of chains from end to end of the mass. Under the influence of

heat, both the sulphur and the carbon expand; but the expansion of the sulphur is nearly ten times as great as that of the carbon, the net result being that the carbon particles are drawn apart, and have fewer points of contact with each other. The number of complete chains is thus diminished, and the resistance of the mass consequently increased.

It is stated in Balfour Stewart's 'Treatise on Heat,' upon the authority of Kopp, that sulphur, after being heated to a certain temperature, contracts instead of expanding. This would account for the fact that, after attaining a certain temperature, the resistance of the mixture begins once more to decrease; for the carbon particles would, when the sulphur contracts, be brought together again.

Several experiments corroborate this explanation of the variation of the resistance. Thus a mixture was made containing 3 parts of shell-lac to 2 of graphite. Though the proportion of carbon was larger than in the sulphur experiments, its resistance was found, as was expected, to be infinite; for the structureless shell-lac penetrated between and completely surrounded the carbon particles. A mixture of paraffin and graphite gave the same result.

A short rod of the usual sulphur-and-graphite compound (20 parts to 9) was fitted with platinum-wire electrodes; and its resistance in the air at 17° was found to be 3170 ohms. The rod was immersed in a beaker of turpentine at the same temperature, and its resistance almost immediately went up about 800 ohms; and in five minutes it was somewhat higher. Though this result did not at first appear to be easily intelligible, it is fully explained by supposing that the liquid penetrated between the sulphur crystals and surrounded the carbon particles. In order to increase the effect, the beaker of turpentine containing the rod was placed under the receiver of an air-pump and the air exhausted. After remaining for a quarter of an hour in a vacuum, air was admitted, and another quarter of an hour was allowed for the action of the atmospheric pressure. At the expiration of this time its resistance was found to have increased to 15,600 ohms, about five times as great as it was originally. The rod was then placed upon blotting-paper; and three days afterwards its resistance was

2970 ohms, the temperature of the air being 16°. This was 200 ohms lower than when it was first made; but the temperature was one degree lower.

Thinking that the oil of turpentine might possibly have had some action on the sulphur, I repeated the experiment with olive-oil. On first immersion, the resistance went up from 2970 to 3150 ohms, and in six minutes to 3770 ohms. It was then left in a vacuum for forty-five minutes, after which the air was admitted, though the effervescence had not even then quite ceased; and when measured, after sufficient interval to allow the oil to penetrate, its resistance had increased to 8140 ohms. The comparative smallness of the effect produced in this latter experiment was probably due to the greater viscidity of the oil.

Lastly, since the behaviour of the sulphur-and-graphite mixture under the influence of heat seemed, like that of the microphone, to depend upon the interaction of contiguous particles of carbon, it was expected that one of the sulphur-cells before described might be used as a telephone-transmitter. This, upon trial, was found to be the case. With a single Leclanché the sounds reproduced in the receiving-telephone were feeble; but well-known nursery-rhymes were easily recognized. When, however, twenty Leclanchés were used, the sounds were much louder and the articulation perfectly distinct. No experiments whatever have yet been made with the view of developing this property; and there can be little doubt that it is capable of extension. It is not impossible that a transmitter constructed upon this principle might be found to be of practical value; and it is entirely different, at least in appearance, from any thing which has been made before.

The sulphur-cell might also perhaps be used as a thermoscope, being simpler and more easy to construct than an ordinary thermopile.

It has recently been proposed to use mixtures of sulphur and graphite for making cheap resistance-boxes. It is needless to point out that the great sensitiveness of such compounds to small changes of temperature renders them very unsuitable for such a purpose.

XI. *On the Fluid Density of certain Metals.* *By* W. Chandler Roberts, *F.R.S., and* T. Wrightson, *Memb. Inst. C.E.**

[Plate V.]

At a Meeting of the Physical Society, on February 12, 1881†, we communicated the results of certain experiments, made with the aid of the oncosimeter, on the fluid density of bismuth, in which we showed that the densities in the fluid and cold solid states are respectively 10·055 and 9·82, the fluid density thus being 2·4 per cent. higher than the cold solid. These determinations correspond closely with results that had been obtained by one of us, using the "cone" method devised by Mr. Mallet‡. For the sake of convenience we here reproduce our results on bismuth.

No. of expt.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including the stem.	Floating effect on first immersion, in troy ounces.	Deduced specific gravity of fluid metal.	Remarks.
31.	2	23·33	9·72	1·0	10·13	Bismuth ball in fluid bismuth.
32.	2·25	22·184	6·99 (iron)	9·3	9·92	Iron ball in fluid bismuth.
33.	do.	33·46	9·755	1·3	10·11	Bismuth ball in fluid bismuth.
34.	do.	33·37	9·757	·6	9·94	do.
35.	do.	33·53	9·774	·7	9·98	do.
36.	do.	22·184	7·02 (iron)	10·2	10·25	Iron ball in fluid bismuth.
					Mean	10·055
					Specific gravity of solid bismuth	9·82

Since these results were published we have extended the

* Read January 28, 1882.

† Proc. Phys. Soc. vol. iv. p. 195; and Phil. Mag. [5] vol. xi. 1881, p. 295.

‡ Proc. Roy. Soc. vol. xxii. p. 366, and vol. xxiii. p. 209.

experiments to the following metals—copper, lead, tin, zinc, silver. The results are now submitted to the Society.

Copper.

Six experiments were made with the oncosimeter* on copper; four of these were made with cast copper balls $2\frac{1}{4}''$ diameter, one with a cast-iron turned ball $2\frac{1}{4}''$ in diameter, and one with a copper ball $3''$ in diameter. The first four were made with a spring that lengthened $\frac{1}{4}$ inch per ounce troy; the last two with a more sensitive spring, giving $\frac{1}{2}$ inch elongation per ounce troy. It will be seen by the accompanying table that the fluid density does not vary much, although, as has just been stated, the conditions were varied.

No. of expt.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including the stem.	Sinking effect on first immersion, in troy ounces.	Deduced specific gravity of fluid metal.	Remarks.
37.	2·25	26·357	8·23	nil.	8·23	Copper ball in fluid copper.
38.	do.	27·005	8·463	·2	8·4	do.
39.	do.	26·25	8·288	·5	8·13	do.
40.	do.	25·923	8·281	·2	8·217	do.
41.	do.	22·186	7·02 (iron)	Floating effect 3·5	8·127	Iron ball in fluid copper.
42.	3	64·237	8·61	Sinking effect 3·0	8·2	Copper ball in fluid copper.
				Mean	8·217	
				Specific gravity of solid copper	8·8	

The mean of these results gives 8·217 as the density of fluid copper. This metal melts at a temperature which exceeds 1000° C., and, when melted in air, absorbs oxygen. We found, for this reason, that it was not possible to obtain trustworthy results by Mallet's method, even though the cone was filled with an atmosphere of coal-gas.

* A description of this instrument was published in the Journal of the Iron and Steel Institute, part 2, 1879, p. 418.

Lead.

Three experiments were made with the oncosimeter, the results being as follows:—

No. of expt.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including the stem.	Sinking effect on first immersion, in troy ounces.	Deduced specific gravity of fluid metal.	Remarks.
43.	3	83·37	10·7	3·5	10·25	Lead ball in fluid lead.
44.	3	83·8	10·8	3·25	10·38	do.
45.	3	84·01	11·07	3·7	10·5	do. Fluid lead getting cold.
				Mean	10·37	
				Specific gravity of solid lead	11·4	

A mean of two experiments on lead, made on Mallet's system, gave 10·65 as the liquid density, the results being 10·63 and 10·66 respectively.

The diagram No. 1 (Plate V.), gives the results of the experiments on lead; and the calculations of fluid density are in each case attached, the point *a* indicating in each the position taken as giving the true initial sinking effect at the moment of immersion.

Tin.

Two experiments were made with the oncosimeter, with the following results:—

No. of expt.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including the stem.	Sinking effect on first immersion, in troy ounces.	Deduced specific gravity of fluid metal.	Remarks.
46.	3	55·66	7·165	1·1	7·02	Tin ball in fluid tin.
47.	Failure.					
48.	3	55·66	7·185	1·2	7·03	do.
				Mean	7·025	
				Specific gravity of solid tin	7·5	

The diagram No. 2 is reduced from the oncosimeter diagram, experiment 48.

A mean of three experiments on tin, made on Mallet's method, gave 6·974 as the liquid density—the results being 6·903, 6·982, and 6·976 respectively.

Zinc.

Three experiments were made with the oncosimeter on this metal, the results being tabulated below:—

No. of expt.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including the stem.	Sinking effect on first immersion, in troy ounces.	Deduced specific gravity of fluid metal.	Remarks.
49.	3	52·52	6·893	2·4	6·57	Zinc ball in fluid zinc.
50.	3	52·53	6·901	3·3	6·47	do.
51.	3	52·32	6·903	3·75	6·4	do.
					Mean ..... 6·48	
Specific gravity of solid zinc 6·8 to 7·2 (Rankine).						

The crucible was kept in the furnace during the three experiments, and maintained as nearly as possible at the same temperature throughout.

Only one determination of this metal has been made by Mallet's method, giving a liquid density of 6·55.

Silver.

We looked with much interest to the experiments on the density of molten silver for several reasons—mainly from the fact that it melts at a high temperature, which has been determined with great care by the late Henri Ste Claire Deville, who in his later experiments on the subject fixed the temperature at 940° C.* We operated on a thousand ounces of silver, which proved on assay to contain 998 parts of pure silver in 1000. We have as yet only secured one trustworthy result, as we found it very difficult so to adjust the temperature of the molten silver as to prevent the silver balls from melting either too rapidly or too slowly. In the experiment No. 52, in which we did secure a result, the metal must have been just about its melting-point, as at the end of four

* *Comptes Rendus*, t. xc. (1880) p. 773.

minutes the silver ball had not entirely melted; the experiment was stopped, however, as the silver began to solidify on the iron stem of the ball.

The diagram No. 3 is reduced from the original; and we have appended the calculation for fluid density, assuming the position of equilibrium at first immersion of the ball to be at point *a*.

The particulars of the experiment are as follows:—

No. of expt.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including the stem.	Sinking effect on first immersion, in troy ounces.	Deduced specific gravity of fluid metal.	Remarks.
52.	3	74·8	10·068	4·1	9·51	Pure silver ball in pure silver.

The liquid density of pure silver, as determined by one of us*, on Mallet's method, from a mean of two experiments, giving respectively 9·447 and 9·476, was 9·46. This confirms the single result obtained by the oncosimeter.

If we now tabulate the mean results of the foregoing experiments, as well as those previously obtained, we shall be able to compare the densities according to the two methods of investigation:—

Fluid density of	By Mallet's method.	By oncosimeter.
Bismuth	10·039	10·055
Copper	.....	8·217
Lead	10·65	10·37
Tin.....	6·974	7·025
Zinc	6·55	6·48
Silver.....	9·46	9·51

The difficulties connected with the working of the oncosimeter are less than those which arise in Mallet's method; and the sources of error are less, the correctness of the result in the latter depending on the metal in the cone being free from air-holes.

It will be seen from the above table that, in the case of

* Roberts, Proc. Roy. Soc. vol. xxiii. p. 493.

the five metals in which both systems were tried, the results correspond as closely as could be expected, taking into consideration the great difficulties of observation at the high temperatures employed. We therefore venture to think that the oncosimeter can be depended upon generally for the determination of the fluid densities of metals, if the experiments are conducted with the necessary care.

Taking therefore the oncosimeter-results as approximately accurate, we find the change of volume of these metals in passing from the cold solid to the liquid state to be as follows:—

Metal.	Specific gravity of solid.	Specific gravity of liquid.	Percentage of change in volume from cold solid to liquid.
Bismuth	9·82	10·055	Decrease of vol. 2·3
Copper	8·8	8·217	Increase of vol. 7·1
Lead	11·4	10·37	do. do. 9·93
Tin	7·5	7·025	do. do. 6·76
Zinc	7·2	6·48	do. do. 11·1
Silver	10·57	9·51	do. do. 11·2
*Iron (No. 4, foundry, Cleveland)	6·95	6·88	do. do. 1·02

The experiments just described lead us to believe that, although the conditions under which they are made may render it impossible to obtain results that are rigidly accurate, still the errors are inconsiderable. It has been urged that the unsoundness or porosity in the casting would disturb the accuracy of the results; but this is provided against in each case by taking the specific gravity of the ball operated on, its iron stem being submerged in water to a point which is afterwards just reached by the molten metal. It has also been suggested that the expansion of the ball, when it enters the fluid metal, causes tension on the metal in the interior of the ball, and that therefore the density of the ball (from which the fluid density is determined) can never be trusted. It must be remembered, however, that the determination of the fluid density is made and automatically registered at the moment of immersion, before the volume of the ball can be practically affected.

* Wrightson, Journal of the Iron and Steel Institute, No. 1 (1880), p. 20.

Since our last paper was read, we have seen that MM. F. Nies and A. Winkelmann* have been investigating the changes in volume of certain metals when melted. Their method will be best understood by a short description of the way in which the metal tin was treated by them.

Tin was melted in a suitable vessel, the melting-point (viz. 226°·5 C.) being carefully maintained. Pieces of tin were then dropped in, and observed first to sink, then to rise before melting—showing that solid tin has a higher specific gravity than the liquid mass, but that when its temperature has been raised to the melting-point, or rather to a certain temperature just below, then it is specifically lighter. In order to determine this relation, they enclosed pieces of copper (having a higher specific gravity than tin) in pieces of tin, and were thus able to increase the specific gravity of the solid piece at will; and although not able to determine directly whether the compound piece was of the same density as the liquid, the latter not being transparent, yet by varying the amount of copper enclosed in the tin, thus forming pieces of a different density, they were enabled to say that it lay between the two limiting values. Compound pieces with varying and known amounts of copper, thus formed, were placed on the surface of the liquid tin for some little time, then dipped under the surface; and it was noted whether they rose again or not. The pieces were each then carefully taken out again and weighed, to ascertain that no part had been melted. This was continued until they found two compound pieces such that, at a temperature just below the melting-point, one would just rise and the other would just sink.

If, then, the relative densities of the liquid tin and the copper at the temperature of liquid tin could be ascertained by experiment, the relative density of the solid tin just below melting-point and the liquid tin can be calculated.

A copper ball was heated to the temperature of the melting tin, and weighed, first in air, then in the liquid tin. The relative densities being thus ascertained, the calculations, which we need not give here, are of a simpler character.

In the case of tin, they found that the liquid is of ·7 per cent.

* *Sitzungsberichte der Akademie der Wissenschaften zu München*, 1881, part 1, p. 63.

greater density than the hot solid at a temperature just below melting-point.

This, so far as it goes, is confirmatory of the results obtained by us. If diagram No 2. be examined, it will be seen that the line of volume rises gradually to the line of equilibrium, indidicating expansion; and just before the ball melts rises above the line, indicating a floating effect, when the temperature approximates to the melting-point.

Tin therefore appears to be similar to iron ; viz. it is at its maximum density when cold, and at its minimum density when at a temperature just below melting, and that the fluid-density is between the two.

The results obtained by MM. Nies and Winkelmann on bismuth will serve to illustrate the degree of approximation of these limiting values.

A piece of bismuth, when allied with a platinum block weighing 21·76 grammes, sank ; and another piece, weighing 35·4 grammes, floated; which is equivalent to stating that the specific gravity of the melting bismuth is between 10·28 and 10·12.

They arrive at the general result that not one of the eight metals they examined will justify the assertion that "bodies contract on becoming solid;" but the experiments rather favour the view that metals when solid, *at a temperature close upon their melting-points*, are less dense than when molten.

Without accepting MM. Nies and Winkelmann's results as final, we do not consider them to be opposed to our own, as theirs relate solely to the ratio of the densities of the solid and liquid metals at as nearly as possible the same temperature, while our experiments were undertaken with a view to determine the actual density of a metal at the *lowest* temperature at which it is perfectly liquid.

XII. *Experiments on the Faure Accumulator.*

By Professors W. E. Ayrton *and* John Perry*.

Having made, at the request of the Faure Accumulator Company, a series of experiments on some of their cells, we have thought that a short account of some of the results obtained

* Read February 25, 1882.

may not be uninteresting to the members of the Physical Society.

The object of the experiments was to ascertain, *first*, the efficiency of a cell—that is, the ratio of the energy given out by it to the energy put into it; *secondly*, the storing-power of a cell; and, *lastly*, whether or not there was a deterioration in its working-powers. To measure the energy put into any electric circuit, we have merely, of course, to take time-readings of the current flowing through the circuit, as well as the difference of potentials between its two extremities. The current in ampères multiplied by the electromotive force in volts and by 44·25, gives the number of foot-pounds per minute that is being put into that part of the circuit as electric energy. For measuring the current we have used throughout our ammeters (short for ampère-meters), and for measuring electromotive force our voltmeters, the latter being employed of course in a shunt circuit.

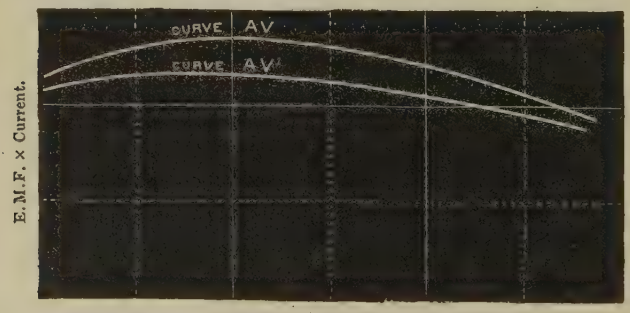
Of the total electric energy put into the circuit, and which is measured, in foot-pounds per minute, by 44·25 AV, a portion will be employed simply in heating the circuit, and the remainder may be utilized in producing useful work. For example, if a time-curve be drawn for 44·25 AV when charging a Faure accumulator, the area of the curve will measure the total energy put into the accumulator in foot-pounds; but of this some portion has been wasted in heating the cell, due to the charging having been more rapid than was absolutely necessary. It was, of course, of considerable importance in our experiments to ascertain what portion of the energy put into the cell was really thus wasted; and to measure this the following experiments were made.

Occasionally the main current was stopped, the shunt current through the voltmeter being left completed. The reading now on the voltmeter gives the difference of potentials produced by the cell itself, whereas the previous reading was the combined difference of potentials produced by the cell and the dynamo-machine charging it. If now a new time-curve be drawn in which the ordinates represent the product of 44·25 AV′, where V′ is the electromotive force of the cell measured on the circuit being broken, and A is the mean value of the current flowing just before breaking and just after

closing the circuit, the area of the new curve will represent that portion of the energy put into the cell which is usefully employed in chemical decomposition. The difference between the areas of these two curves represents, then, the amount of energy wasted in heating the cell in foot-pounds.

Again, on discharging the cell, experiments of a similar nature have to be made. The product 44·25 AV represents the number of foot-pounds of work per minute the cell is producing in the external circuit, V being the difference of potentials between the two poles of the cell while it is discharging; but, in addition, there is a certain amount of energy which is being expended in heating the cell itself during discharge.

This, as before, may be ascertained by breaking the main circuit, leaving the shunt-voltmeter circuit completed. The reading on the voltmeter V′ now indicates the real electromotive force of the accumulator during discharge; whereas the previous reading, obtained just before breaking the circuit, represents merely the fraction of the total electromotive force employed in sending the current through the external resistance. If a time-curve be drawn with its ordinates proportional to 44·25 AV′, where A is the mean value of the current just before breaking and just after closing the circuit, its area will represent the total number of foot-pounds of energy per minute being given out by the cell; and the difference between the areas of the last two curves will represent the number of foot-pounds of energy employed in heating the cell itself. It is to be noticed that during charging V′ is less than V, whereas on discharging V′ is greater than V.



An examination of thirty-five sheets of time-curves, which

we have drawn from the experiments we made, shows that, in charging, the curve for AV rises at first; and as it rises more rapidly than that for AV′, this means an increase in the resistance of the accumulator.

As the charging continues, the two curves for AV and AV′ approach one another, showing that the internal resistance of the accumulator diminishes again. On the other hand, at the end of a long discharge the curve for AV falls more rapidly than that for AV′, due to an increase in the internal resistance. Now our experiments show a great constancy in the electromotive force of a Faure cell, and that the falling-off in discharging which occurs during a very rapid discharge, or at the end of a long discharge, is due more to an increase in the internal resistance of the accumulator than to a diminution in the electromotive force, which our methods of experimenting above described enable us to separate and measure independently. But, whether discharging rapidly or whether discharging slowly, there is a most curious resuscitating-power in the cell, which, if disregarded, will cause totally erroneous underestimates to be made of the efficiency of the cell.

This resuscitating-power is more marked for rapid discharges than for slower ones. In the case, for example, of an extremely rapid discharge, we found that when the flow had become apparently so feeble that the cell appeared totally discharged, leaving the poles of the cells insulated caused three times as much electric energy to be given out all together in the second discharge as had been given out in the first. And even when several days are taken to discharge the cell—and we may mention that we have had continuous observations made day and night for several days in certain cases—this resuscitating-power is wonderfully marked. An insulation of a few hours will cause the energy given off per minute on redischarging to be eight to ten times as great as it was before insulation. Indeed on one occasion, after a cell had apparently nearly discharged itself, it was left shortcircuited with a thick wire for half an hour, then insulated all night, when the number of foot-pounds of work per minute given off at the commencement of the discharge the following morning was found to be ten times as great as it was on the previous evening, and a greater amount of energy was actually taken from it in the

second discharge than in the first. This phenomenon gives the Faure accumulators a great value for tramcar propulsion, since, as is well known, it is just on starting after stopping that the strain on the horses is so great.

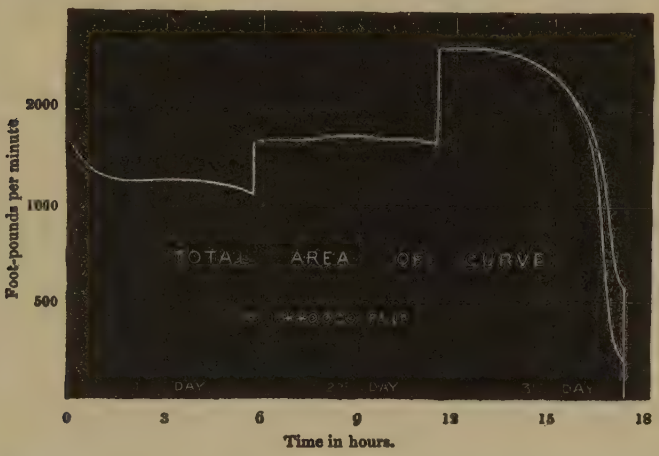
Efficiency.—To determine the efficiency of cells we commence with them empty, or at least as empty as many hours' shortcircuiting with a thick wire could make them. We then measured the total amount of energy put in and the total amount subsequently given out, and we found that, for charges up to a million foot-pounds put into the cell and discharged with an average current of 17 ampères, the loss in charging and discharging combined may not exceed 18 per cent. Indeed, for very slow discharges the loss in charging and discharging combined in some of our experiments has been as low as 10 per cent.

Storing-power.—It is a little difficult to measure the maximum storing-capacity of the cell at the same time that measurements are made of its efficiency, because in the latter case we must take care that we do not put in more electric energy than the cell can hold; on the other hand, if precautions are taken to avoid overcharging, it is a little difficult to ensure that the full charge has been put in. We have therefore separated our experiments for measuring the efficiency from those employed to ascertain the storing-power.

Let us take a single example of the storing-capacity. A certain cell containing 81 lb. of lead and red lead was charged and then discharged, the discharge lasting eighteen hours—six hours on three successive days; and it was found that the total discharge represented an amount of electric energy exceeding 1,440,000 foot-pounds of work. This is equivalent to one horse-power for three quarters of an hour, or 18,000 foot-pounds of work stored per pound weight of lead and red lead. The curve shows graphically the results of the discharge.

Horizontal distances represent time in minutes, and vertical distances foot-pounds per minute of energy given out by the cell, and the area of the curve therefore the total work given out. On the second day we made it give out energy more rapidly than the first, and on the third more rapidly than on the second, this being done of course by diminishing the total resistance in circuit. During the last day we were discharging

with a current of about 25 ampères. And this cell, like the others, showed, on being insulated after having been apparently



totally discharged, that there was still a large charge stored up; hence the numbers given above for the capacity are probably under the total value.

Deterioration.—As to deterioration, two months constant charging and discharging of the two accumulators under test showed no signs of deterioration.

XIII. *A Simplified Dispersion-Photometer.*

By Professors W. E. Ayrton *and* John Perry*.

It will be in the recollection of the Members that in 1879 we described to the Society a dispersion-photometer which enabled measurements to be made of the intensity of the strongest electric light in a small room and for the rays coming from the electric light at any angle—two essentials which appeared to us necessary in an electric-light photometer. The principle of this photometer consisted in our use of a concave lens to weaken the strength of the light, so as to make the illumination of a screen comparable with the illumination of a standard candle, instead of keeping the lamp a distance of 50 or 100 feet away, which was the plan in use until that time.

* Read February 25, 1882.

We exhibit now five successive forms of the instrument, which illustrate the history of its development to the present time.

1. The first of these is very nearly the same as that described in our former paper, with the exception that we discarded the use of a long screw (shown in our original figure) for adjusting the position of the lens—as we found that a very easy adjustment might be effected with the fingers, the tension of the bellows part making an automatic clutch which fixed the lens-slide in any position.

2. The second specimen is on the same principle, only that telescope-tubes are used instead of a wooden frame and a bellows. Instead of the lens part alone tilting when the elevated or depressed light has to be examined, the candle-box is here made to tilt also, the candle being supported in gimbals so that it may remain vertical for every angle of elevation.

3. The third specimen is on pretty much the same principle; but as we found a difficulty in comparing two illuminated disks whose centres were some distance apart, we arranged in front of these disks two mirrors, which enable us to make the comparison between two illuminated semicircles having the same diameter. The difficulty of adjusting the lens and making a comparison of the illuminations, and reading the scale, without moving one's head, in all these early instruments led us to the

4th form, which is probably familiar to the Members, as it was exhibited at Paris and largely used there for measurements. In this the candle-box and the lens-box are placed end to end, the lens is fixed in a wooden piston which moves in its hollow square box, which is lined with velvet; and the lens shows its position by a pointer moving over the scale outside. The pointer projects from the inside of the wooden cylinder at any point of a long slot, whose sides are made of india-rubber tubing, so that no extraneous light can reach the illuminated screen. A little handle working a rack and pinion enables the lens to be placed in any position. Through a hole at the side the two screens can be viewed reflected in two mirrors, inclined to one another in the space between the candle-box and the lens-cylinder; and the illuminated papers are viewed as two semicircles having a common diameter. In front of this hole we have slides of red and green glass ; so that,

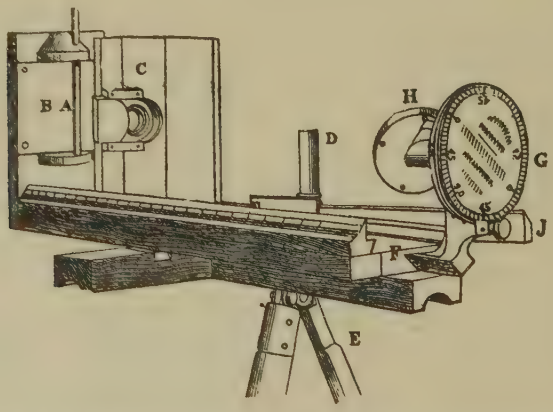
as our custom has always been, we make two measurements—one a comparison of the ruby-red light of the lamp examined with the red light of the candle, and another of the green lights. This instrument differed from the earlier forms in not requiring any calculation to be made of the strength of the light; that is, the reading of the pointer was not merely a reading of its distance from the screen, but it was a reading in standard candles of the power of the light. Three such scales were placed on the instrument; and there were three certain distances at which the lamp had to be placed for examination. The tilting-arrangement was of course different from that of the earlier forms.

As the instrument had by this time (the end of last year) come into a rather extensive practical use, we had opportunities of seeing that, as an instrument to be used by unscientific persons, it was not yet in a perfect condition, in spite of the many changes that had been made in its construction. The most important difficulty was due to the fact that a slight lateral change in the position of the observer's eye caused the apparent illumination of the screens to vary. Being aware of this fact ourselves, we maintained a certain fixed position of the eye when making observations; but the instrument could not at once be used by persons not accustomed to make delicate experiments.

5. The fifth form, which we now present to the Society, is the outcome of our labours on this subject. We have all along seen the disadvantage of using the Bouguer's two-screen method, since, when lights are examined that have passed through tissue or tracing-paper, a very slight change in the position of the observer's eye makes a very great difference in the apparent illumination, whereas, using Rumford's method, when a sheet of white blotting-paper is employed as a screen very considerable changes in the position of the eye produce no change in the apparent illumination—a result, however, which is not attainable when ordinary drawing-paper is used as the screen. If, however, Rumford's method is to be used to measure the rays coming at different angles from an electric light, a mirror must be employed to reflect them successively onto the same screen; and if used in the ordinary way, the angle of incidence of the rays on the mirror will be

different in different cases. Now the difficulty that always met us arose from the inequality of the reflecting-power of an ordinary mirror for rays falling on it at different angles of incidence. We have, however, completely overcome this difficulty in an extremely simple way, by causing the mirror to turn about a horizontal axis inclined at 45° to its plane, and the whole photometer to turn about a vertical axis. With this arrangement the angle of incidence, and consequently the proportional absorption, is the same whatever be the inclination of the rays coming from the lamp to the mirror; and, further, the angle being 45°, the amount of rotation of the mirror about its horizontal axis necessary to enable measurements to be made of rays coming at any angle, after measurements have been made of the horizontal beam, is exactly equal to the inclination of the beam in question.

Using Rumford's method in this latest form of our photometer, we are to a great extent independent of the presence of other sources of illumination of the screen, so that the apparatus need not be enclosed in a box. At the same time, however, the sensibility of the test is much increased by placing a shade to prevent the electric light shining directly onto the screen. On this screen of blotting-paper, B, is thrown the shadow of a black rod, A, placed in front of it, by a candle in the candle-holder, D.



Now it is well known that if an electric light is also allowed to illuminate this screen, and to throw a second shadow of the

rod A on the paper, and if the candle is adjusted at such a distance that the two shadows are of equal intensity, the strength of the light is to that of the candle in the ratio of the squares of their distances from their respective shadows. But instead of allowing the strong light to pass directly to the screen, we cause it to pass through the concave lens in the sliding wooden frame C. A pointer on this slide tells the distance of the lens from the screen. As you are all aware, the weakening of light-intensity produced by the lens enables us to leave our electric lamp within a few feet of the instrument. We have experimentally found that there is no appreciable loss of light in passing through the lens. The candle slides on the bar J; and its distance from its shadow is shown by a pointer on a scale. If f is the focal length of the lens, D the distance of the electric light from the paper-screen, d the distance of the centre of the lens from the screen, and c that of the candle when the shadows show equal illumination, then, if L is the strength of the examined source of light in standard candles,

$$\sqrt{\mathrm{L}} = \frac{\mathrm{D}-d}{c}\left\{1 + d\left(\frac{1}{f} + \frac{1}{\mathrm{D}-d}\right)\right\},$$

or

$$\mathrm{L} = \frac{1}{c^2}\left\{\mathrm{D} + \frac{d(\mathrm{D}-d)}{f}\right\}^2.$$

For our own use we prefer to employ the formula; but as all the common instruments which have hitherto been manufactured have lenses whose focal length is 4 inches, we have prepared a table, a copy of which is sent out along with each instrument, in which the value of L is given for various values of D, d, and c. Using this table, it is necessary to have the lamp at either 60, 120, or 300 inches from the screen; the candle is either at 10, 14·14, or 20 inches from the screen; and the table is made out for every half inch of the lens-scale. But inasmuch as we find that the improved arrangement of the mirror already referred to constitutes perhaps the most useful part of the instrument, and as the use of this improvement involves many alterations of D, the manufacturer proposes in future not to furnish any table of values of L unless specially asked for.

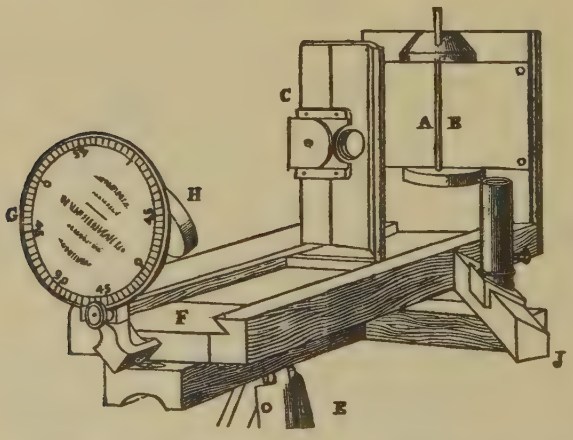
H is the plane silvered-glass mirror which makes the angle

of 45° with the axis of the lens, and with the axis about which the mirror itself is free to revolve. As already explained, a ray of light reflected from the mirror and passing through the centre of the lens must, for any position of the mirror, have an angle of incidence of 45°, and so must experience the same amount of absorption, from whatever direction it may have come to the mirror. Further, this angle being 45°, a fixed pointer marks on the graduated circle G, which moves with the mirror, the angle which any ray we may be examining makes with the horizontal.

In this instrument we find that from 30 to 34 per cent. of the incident light at 45° is absorbed, whether this light is of ruby-red or signal-green colour; so that we have the easy practical rule for all cases—add one half to the measured intensity of light reflected.

We need not here refer to the fact that, when investigating the efficiency of an electric lamp, we always measure the horse-power given electrically to the lamp simultaneously with the photometric measurement.

The lamp is suspended in such a way that it can readily be placed at any elevation. The frame of the tripod-stand is first levelled. A pin at F, directly underneath the centre of the



mirror, passes through the base of the photometer and fits into a hole in the top of the tripod-stand. The photometer, by turning round this pin, can, without producing any change in

the distance of the centre of the mirror from the lamp, and therefore without changing the distance from the screen to the lamp, receive the small horizontal motion necessary for the adjustment of a new inclination of the rays coming from the electric light, without any alteration of the distance of the centre of the mirror from the lamp. The divided circle is clamped with the index at 0°; the lamp is lowered or raised till the illuminated disk formed by the reflected light, passing afterwards through the lens, is in the middle of the paper screen. A little sliding shutter with a fine hole in its centre, seen in the figure, enables a very exact adjustment to be made; but in practice we find that we get sufficient accuracy without the use of the shutter. We now measure the distance from lamp to centre of mirror in inches. Equalizing the intensities of the two shadows by adjusting the lens-slide when looking at them through red or green glass, we now note the lens- and candle-readings; and we repeat these operations, changing from red to green and green to red about five times in a minute. The lamp is now raised or lowered and fixed in any position; a few seconds suffice to turn the mirror so that it sends its centre ray exactly through the centre of the lens. The distance from screen to mirror in this instrument being 22 inches, if δ is the distance from centre of mirror to vertical from lamp, and if θ is the angle of elevation, then

$$D = 22 + \delta \sec \theta.$$

Using this value of D in the formula above, and adding one half to the strength of the light to make up for absorption, the true intensity of the light in standard candles can be ascertained. We find in practice that, if an electric light is moderately steady, ten measurements may be made, with some confidence in their accuracy, in two minutes; and the light may be measured in ten different positions, from an angle of depression of 60° to an angle of elevation of 60°, 100 observations being taken, in less than half an hour.

We may mention one very important result we have been led to by the systematic employment of a photometer which can be used close to the electric light; and that is the large amount of absorption that occurs on certain days when the rays from strong electric lights, and especially the green rays, pass through the air which appears to the eye perfectly clear.

At first we were inclined to think the higher results for the candle-power of a lamp obtained with our dispersion-photometer than those obtained with an ordinary distance-photometer were due to some error in our photometer itself; but we have since ascertained that this is due to the absorption of the air—because we find that, if simultaneous measurements are made with ordinary Rumford's photometers, each without lens or mirror, placed at different distances from the lamp in the same azimuth and in the same horizontal plane, the nearer one gives, as a rule, the highest readings; and the difference is the greater the stronger the light, and is greater if the light be examined at each photometer with green glass.

XIV. *Notes on Thermometry.* *By* F. D. Brown, *B.Sc.*, *Demonstrator of Chemistry at the University Museum, Oxford.*

[Plate VI.]

Some years ago, when I determined to try and find out something about the attractive forces which the atoms and molecules seem to possess, by studying the effects of heat upon chemical substances and upon mixtures of such substances, I was led to the conviction that, if the work which I proposed to do was to be of any permanent use, I should be obliged to take many and minute precautions regarding the measurement of temperatures—a measurement which, owing to the peculiarities of mercurial and other thermometers, is so liable to error. In order to learn how best to use my thermometers, and how to refer their readings to a satisfactory standard, I made a considerable number of experiments. At the time when these experiments were made I imagined that the subject of thermometry, although presenting many difficulties to my mind, had been thoroughly worked out by others, and therefore that a printed record of my observations would be generally deemed to be of little utility. The recent publication of a paper by Dr. E. J. Mills (Edin. Roy. Soc. Trans. 1880), of one by Professors T. E. Thorpe and Rücker (Phil. Mag. [5] xii. p. 1), and more especially of a report by M. Pernet (*Mém. et Travaux du Bur. inter. des poids et mes.* i. 1881, pp. 1–52), has led me to change my opinion, and to

think that there still remain many points connected with thermometers about which not only I, but others also, would be glad to have more certain information. Acting upon this belief, I have put together in the following pages some of the results of my experiments.

The Mercurial Thermometer as a Standard.

I was soon convinced that any attempt to express temperatures in degrees of an ideal absolute thermometer, or even to refer them correctly to the readings of an air-thermometer, would involve a most extensive and wearisome investigation, which would postpone indefinitely the work I wished to do. To avoid this substitution of the means for the end, I decided to construct a mercurial thermometer and to use it as a standard, keeping it until such time as the progress of our knowledge should render its comparison with the air-thermometer a matter of less difficulty.

As a mercurial thermometer is very liable to be broken, I first wanted to know whether this instrument fulfilled the primary condition of a true standard, of being capable of reproduction when lost or destroyed. With this end in view, I made two thermometers at different times, and wholly independently one of the other, and compared their readings. To those who may wish at any time to construct a mercurial thermometer without the elaborate appliances ordinarily employed, but in which absolute confidence may be placed, the following details may be of interest:—

A capillary tube of medium bore, about 800 millimetres long, free from all flaws, and having as uniform a section as possible, is provided with a millimetre-scale of 600 divisions. The etching of this scale is a matter of great consequence: it very frequently happens that the divisions on glass tubes are not of exactly equal length, but that, owing to some defect in the dividing-engine or some movement of the tube while undergoing the process of division, some of the divisions are so much longer or shorter than the rest as seriously to interfere with the subsequent process of calibration. Even when all the lines are equidistant, they are often so thick, and present so irregular an outline when viewed through a telescope, that it is impossible to fix upon any particular point as that repre-

sented by the dividing-line. The tubes I employed were selected and divided with special care by Mr. Casella, the lines being perfectly straight, less than 0·4 millim. in thickness, and in all cases equidistant.

As a glass tube, however carefully selected, is never of uniform bore, it is necessary to ascertain the relative capacities of the several divisions of the tube, or, in other words, to "calibrate" it. As is well known, this is easily done by placing a thread of mercury in successive positions along the tube and observing its length, the mean capacity of the divisions occupied by the thread being, of course, inversely proportional to that length. In this way, and by adopting the plan of correcting the position of the thread suggested by Dr. Mills in the paper above referred to, which plan he had been kind enough previously to communicate to me privately, a table is readily constructed showing the volume of the tube from the line marked 0 to any line marked n, and also the value of the succeeding division. The only difficulty connected with this process is the accurate measurement of the length of the thread of mercury in its several positions. It is true that this may easily be done with a dividing-engine or some similar instrument, such as a cathetometer provided with a micrometer eyepiece and placed horizontally. As, however, reliable instruments of this class are exceedingly costly, I designed a small piece of apparatus for the purpose, which has proved so convenient and useful that I venture to describe it here.

A mahogany board, B B (Pl. VI. fig. 1), about 18 inches long and 4 inches wide, is provided with a groove, G G, of the shape shown in the section (fig. 1 *a*); a piece of gun-metal, about 5 inches long and $\frac{1}{4}$ inch thick, slides in this groove with some little difficulty—the friction, which is produced by the spring *f f*, being necessary to retain the plate rigidly in any given position. The plate, D, is provided with a slot, *e e*, and a millimetre-scale, S S, the dividing lines of which must, like those of the tube to be calibrated, be very fine and truly equidistant. The piece of gun-metal, E, which is provided with a vernier, carries the reading-microscope, M, and can be moved along S S by means of the rack and pinion *p*; the movement is rendered smooth and free from lateral displacement by the spring *c*, which causes the ends of E to remain always in contact with the

straight edge of the slot. The thermometer-tube is fixed with suitable screws under the path of the microscope, so that the length of a thread of mercury can be easily measured by placing the microscope so that its cross wire coincides first with one end of the thread and then with the other, and noting on the scale the distance between the two positions.

The millimetres of the brass scale and those of the tube, if marked off by different makers, will often differ a little in length; hence it is generally more satisfactory to obtain from the glass scale the number of whole divisions occupied by the thread, and to measure the terminal fractions only by the microscope.

Since the line on the outside of the tube is nearer the eye than the thread of mercury inside the tube, it is clear that when the microscope is adjusted to view the end of the thread, and is then moved along until the cross wire coincides with the nearest line, this last will be out of focus, and either the whole microscope must be raised up or the distance between the object-glass and eyepiece altered. Now, unless the instrument be constructed with great solidity, and much care be taken to fit accurately all the moving parts, this adjustment will probably alter the position of the optical axis, and so render the measurements inaccurate. To avoid this difficulty, I added a half-lens, L, fitted in the ordinary way on a brass tube sliding on the end of the microscope. This lens of course brings the focus of half the field nearer the object-glass; so that, by properly adjusting it, the divisions are seen through the half-lens at the same time that the mercury is observed through the unprotected part of the object-glass. In this way all disturbance of the microscope is avoided throughout the calibration, which is thus carried out with much greater comfort and accuracy.

Two tubes were calibrated with this apparatus, and tables of their volumes from the first division compiled; they were then furnished with bulbs, filled with mercury, and sealed up in such a manner that they formed thermometers capable of indicating temperatures between 0° and 150° C. The fixed points of the two thermometers having been determined with the precautions indicated below, tables showing the temperatures corresponding to the readings of the scale were

made in the usual manner; the two instruments were then compared together, either in a large tank of water which was kept well stirred, or in the steam-apparatus which I described to the Physical Society at the time when these experiments were made. Before a series of readings were taken, both thermometers were heated for at least half an hour in steam, while their zero-points were observed after the series was completed. The numbers given in the following table show that the two thermometers gave practically identical readings. It would seem, therefore, that the mercurial thermometer, when carefully made and systematically heated, does really possess that valuable property of a standard, of being capable of exact reproduction.

Reading of AS, corrected for index-error.	Reading of BS, corrected for index-error.	Corresponding value of AS, in degrees.	Corresponding value of BS, in degrees.	Difference.
58·55	70·64	14·30	14·29	−·01
134·33	150·11	33·69	33·71	+·02
179·69	197·20	45·29	45·30	+·01
321·97	345·96	81·88	81·88	·00
23·42	33·74	5·28	5·28	·00
26·33	36·83	6·03	6·04	+·01
30·07	40·63	6·99	6·97	−·02
33·76	44·57	7·94	7·93	−·01
43·32	54·70	10·40	10·40	·00
47·98	59·60	11·59	11·59	·00
69·42	82·13	17·09	17·09	·00
91·61	105·52	22·78	22·79	+·01

Determination of the Zero-point.

In most books on physics it is stated that, in order to obtain the zero-point of a thermometer, the instrument should be placed in a vessel filled with broken ice and provided with holes at the bottom, through which the water formed by the melting of the ice may escape. In order to learn whether this method is the best possible, the following experiments were made:—A number of tin pots, about 7 inches high and 4 inches in diameter, were obtained, and holes made in the bottoms of two or three of them. A large block of ice was broken up into small fragments, which were well mixed up, so as to render the whole perfectly uniform in character. One of the tin pots, which we will call A, was filled with

some of this ice, which had been washed in a funnel with ordinary water; A was then filled up with water, so as to form a mixture in which the ice largely predominated. A second tin, B, was filled with some more of the ice, which had been washed with ordinary water in the same way; B, however, had holes at the bottom, and the water formed by the fusion of the ice thus drained away. A third tin, C, contained some of the same ice, which had been washed in a funnel with distilled water, and then mixed with distilled water in the same way as in A the ice was mixed with ordinary water. In a fourth tin, D, which was provided with holes, some ice was placed which had been washed with distilled water. Finally a quantity of distilled water was artificially frozen the ice broken up into small pieces, washed, and mixed with distilled water in a fifth tin, E. A thermometer with a long narrow bulb, and with a stem divided into millimetres, was carefully inserted into each tin in succession, and readings taken with a cathetometer. About 17 millim. of the scale were equivalent to one degree Centigrade. In A the readings soon became constant at 1°·00; in B the readings varied considerably for about half an hour, but finally became constant at 1°·12; in C the thermometer became rapidly constant at 1°·16; in D the readings became constant after a short time at 1°·06; in E the readings did not vary after the first four or five minutes, remaining at 0°·64.

At the end of these observations, which occupied nearly two hours, the thermometer was replaced in A, where the mercury rapidly assumed the same position as before, viz. 1°·00. Seeing that, with the exception of E, the greatest difference in the readings does not amount to 0°·01 C., we may fairly draw the following conclusions:—First, that a constant temperature is more rapidly and certainly obtained with a mixture of ice and water than with ice alone; secondly, that the temperature thus obtained is really that of melting ice; thirdly, that it is preferable to wash and mix the ice with distilled water, ordinary water tending to lower the temperature, though to an insignificant extent.

With the view of seeing whether different varieties of ice gave the same results, two specimens of block ice and one of the rough thin ice collected in winter near London were

obtained, while two cylinders of distilled-water ice were artificially produced. These were all broken up separately into small pieces, washed with distilled water, and then mixed with the same in five tins, A, B, C, D, E. The thermometer placed in these tins marked 1°·30, 1°·34, 1°·26, 1°·30, and 1°·27 respectively (these numbers are not comparable with the former, as the experiments were made a month or so later, when the zero of the thermometer had altered its position). These experiments showed that distilled-water ice gave the same results as ordinary ice, and that the melting-point of different specimens of ice, when mixed with distilled water, was the same within 0°·005 C. The exceptionally low reading obtained with the tin E in the first series of experiments was probably due to the fact that the ice, having been made by means of a freezing-mixture, was not at its maximum temperature.

In subsequent determinations of the zero of thermometers I have always used ordinary block ice, washed and mixed with sufficient distilled water just to fill up the spaces between the pieces, and have not allowed the water to drain away. These results are in accord with those obtained by M. Pernet.

Zero-movements, and Substitution of the Determination of the Steam-point for that of the Zero-point.

In considering the well-worn question of the zero-movements of thermometers, it is important to distinguish between its practical and theoretical aspects. To make a study of zero-movements from an abstract point of view, to find out equations expressing these movements under different circumstances and with different thermometers, to learn that when a certain thermometer has been subjected to a certain series of temperatures at certain intervals of time its indications on next changing its temperature will be affected with a certain index error, may possibly be of some utility, but it does not aid us much in the endeavour to free the readings of thermometers from the errors with which they are surrounded. When once we have acquired the information that a thermometer subjected only to those changes of temperature which are due to the weather exhibits a gradual rise of zero, that the rise thus taking place in a given time diminishes as the age of the thermometer increases, but differs for different thermometers, when

we also know that a thermometer subjected to a high temperature after a considerable period of rest exhibits a decrease in its zero-reading, dependent on the thermometer itself and also on its previous history,—we know all, or nearly all, that we can put to practical use.

Thus, for example, the thermometer attached to my standard barometer was verified at Kew Observatory when it was first supplied to me, some four or five years ago. Since then I have from time to time observed its reading in melting ice, and have modified accordingly the correction to be applied to it. Now, no observations of other thermometers—no curves or equations representing their zero-movements—could be of any assistance to me in this matter. I knew that the zero would probably rise, and that the amount of the rise would not be the same in my case as in that of others, and that, therefore I must obtain the index-error experimentally. I also knew, that if I boiled the thermometer I should cause irregular changes in the position of the zero; and as there was no necessity for the operation, I avoided boiling it. But if by mischance it had fallen in boiling water, no equations representing the zero-movements of other thermometers would have told me exactly what had happened to mine; I should simply have been obliged to observe its index-error more frequently than before the accident happened.

The question which seems to me to be of the greatest importance with regard to zero-movements is, how we can best reduce the trouble which they cause us. In the case of all meteorological and clinical thermometers, where the changes of temperature are small, as in the above case, it is evident that all we can or need do is to protect the instrument from unnecessary changes of temperature. When, on the contrary, our observations extend over wide ranges of temperature, the difficulties increase considerably. Suppose, for example, that I want to use a thermometer to indicate accurately a series of temperatures between 70° and 90°. It is obvious that if I observe the index-error beforehand, and apply the correction thus obtained to my readings, I shall not be doing right; for the very heating of the thermometer to 70°–90° will have altered the index-error. But if, on the other hand, I first heat the thermometer to 100°, then ascertain its index-error, then make my experi-

ments with it, and finally observe its reading in ice a second time, I shall be tolerably certain, if the index-error is the same at the end as at the beginning of the experiment, that no variation has occurred during the observations.

In most laboratories, however, the frequent determination of the zero-point of a thermometer involves a considerable expenditure of labour: ice has to be purchased, broken up into small pieces, washed, and placed in a suitable vessel. All this requires no little time, and has, moreover, to be repeated at every determination, since the broken ice melts away in the interval. On the other hand, the apparatus for the observation of the steam-point is always in readiness; if, therefore, no greater error arises when the index-error is determined before and after the experiments by means of the steam-point, a great saving of time will be effected, without any corresponding loss of accuracy.

When the temperatures to which the thermometer is to be exposed are greater than 100°, the instrument should be heated for some time to the highest probable temperature before the steam-point is observed for the first time. In this way the lowering of the zero which takes place when a thermometer is heated from 100° to some higher temperature, to which it has not been exposed for some time previously, is effected first of all, and does not take place during the experiments, as it otherwise would.

The only objection which can be raised to this method is that, when some at least of the temperatures to be measured are below 100°, it is possible that the steam-point, which is lowered by the first heating in steam, rises again during the experiments (that is, when the thermometer is at a lower temperature), and then, by the second heating in steam, is again brought to the same position as at first. In this way the observations in steam, although concordant, would not give the true index-correction to be applied to the readings. That the error which thus arises is of no importance is, I think, rendered probable by the following considerations:— The gradual rise of the zero of a thermometer receives its most natural explanation when it is supposed that the glass bulb, after having been heated and somewhat quickly cooled, is in a state of strain which causes it to have a larger capacity

than it would have if no such strain existed. As time goes on, and more especially as the thermometer is subjected to small fluctuations of temperature, the particles of the glass gradually yield to the forces which are acting upon them, and take up new and more suitable positions. These molecular movements result in a gradual diminution of the capacity of the bulb, and consequently in a rise of the zero. Now it is evident that, if a certain state of strain is set up when a thermometer is cooled from 100° to 0°, when it is cooled from 100° to some intermediate temperature t the strain set up will be less considerable; there will therefore be a greater tendency for the zero to rise when the thermometer is placed in melting ice than when it is subjected to the temperature t. Consequently, if it be found that, when a thermometer after being heated in steam is placed in ice, no change of the zero takes place for three or four hours afterwards, we may legitimately conclude that, if the thermometer were maintained for the same time at the temperature t, no movement of the zero would occur. I have frequently kept recently-heated thermometers in melting ice for several hours, renewing the ice when necessary; and I have always observed, with all of my instruments, that no change took place for the first three hours, and that during the next two or three hours the rise was extremely small. It follows, therefore, that if in any series of observations lasting more than three hours the thermometer be heated in steam at the end of every third hour, there will be no uncertainty as to the position of the zero; that if the experiments be carried on continuously for six hours, a slight rise of the zero may occur during the last part of the time, but that this rise will not amount to more than one or two hundredths of a degree.

Correction for the Exposed Portion of the Thread.

When a thermometer is only partially immersed in the medium of which the temperature is to be observed, the readings become subject to an error which arises from the fact that a part of the thread of mercury, together with the corresponding portion of the stem, are at a temperature different from that of the bulb and immersed portion of the stem. The correction, C, usually applied in this case is given

by the formula

$$C = m(T - t)N, \quad \ldots\ldots \quad (1)$$

where T = the reading of the thermometer,

t = the temperature of the exposed portion,

N = the number of exposed divisions of the stem which are filled with mercury,

m = the apparent expansion of mercury in glass.

This formula is founded on the assumption that the error in the reading has no other cause than the comparatively unexpanded condition of a portion of the thread and stem.

The apparent expansion of mercury in glass, as obtained from Regnault's experiments, is about ·0001545; but it differs, of course, for different specimens of glass. When this number is employed in the above formula, the values of C obtained are generally believed to be too large; indeed a little reflection will convince us that this must be the case whenever the temperature of the exposed portion is merely measured by placing another thermometer with its bulb halfway up it. This second thermometer evidently measures the temperature of the ascending stream of warm air around the stem; if the stem of the chief thermometer were subjected to the heating influence of this stream, and to no other, its temperature would be rightly given by the subsidiary thermometer; but the thermal conduction along the thread of mercury and along the glass stem must necessarily raise the lower part of the exposed stem to a temperature higher than that indicated by the subsidiary thermometer. The value of $(T - t)$ therefore is too great, and consequently also that of C.

In order to meet this difficulty, Dr. Mills, instead of endeavouring to give to $(T - t)$ its proper value, has made a large number of experiments with different thermometers with a view to assign a more satisfactory value to m, and has thus been led to draw the following conclusions:—The value ·0001545 of the coefficient m is invariably too great. This coefficient varies with the thermometer employed, and also with the number of divisions of the thread exposed; so that, instead of assigning one definite value to m for each thermometer, we must give it a value

$$m = \alpha + \beta N,$$

where α and β must be determined for each thermometer.

Professors Thorpe and Rücker, on the other hand, while admitting that the value $m = 0001545$ may be generally too large, maintain that it is sufficient to replace it by some other single number, and that the employment of the varying coefficients $\alpha + \beta N$ is unnecessary; they support this opinion by showing that in Dr. Mills's own experiments the alterations in the value of C, caused by the introduction of the term βN, do not amount to more than one or two hundredths of a degree, and are therefore insignificant. Dr. Mills, replying to this, states that the change in the correction C brought about by the term βN often amounts to so many hundredths of a degree that it cannot be neglected.

Now it is clear that by merely placing a second thermometer halfway up the exposed thread, only the roughest idea is obtained of the real temperature of the thread. Suppose, for example, that $T = 100°$, and that t is taken at 15°, being subject to an error of 5°: the value of $(T-t)$, which is 85, will be subject to an error of 5°, or about 6 per cent. What, therefore, can be the use of attempting to determine the coefficient β, of which the value would appear ordinarily to be about 0·0000002, when so great a source of error is left unprovided for?

In all experiments in which I have had occasion to use mercurial thermometers, I have endeavoured to avoid any correction for the exposed thread, by making the apparatus and thermometers employed of such relative dimensions that the whole thread and bulb, except the topmost division, are at the same temperature. When this is impossible, and when the experiments require such extreme accuracy, it seems to me that the first thing to be done is to surround the exposed portion of the thread with a current of running water, and so, while preserving it from the uncertain effects of conduction, radiation, &c., to render possible the observation of its exact temperature. The value of $(T-t)$ being thus correctly measured, that of m is found to be constant for all values of N, and to differ but little from 0·001545. It varies, however, with different thermometers.

The following experiments show most distinctly the truth of this statement:—

One of the standard thermometers mentioned in the first

section of this communication was partially surrounded by a glass tube, *a b* (fig. 2), about an inch in diameter; this tube was closed at the bottom with a piece of good cork, about 8 millim. thick, through which the stem of the thermometer passed. The upper end of the tube *a b* was fitted with a cork, in which were four holes—one for the stem of the chief thermometer, a second for a thermometer to indicate the temperature of the water contained in the tube, while through the two others passed the tubes by means of which the current of water was maintained. The thermometer thus furnished was fixed vertically in the ordinary apparatus, A, for determining the 100°-point of thermometers. The open end of A was closed with a thin disk of brass, with a small central hole, through which the thermometer passed. One degree was equal to about four divisions of the millimetre-scale of the thermometer, the readings of which were observed with a cathetometer, and the fractions of a division measured with that instrument. It was found that the readings of the thermometer under these conditions were correct to ·02 of a millimetre, or ·005 of a degree. The numbers given below are the means of three readings, which, however, were nearly always identical. The thermometer in the water was graduated to fifths of a degree, and had been compared with the standard.

The chief thermometer was first heated in the steam for an hour, with two or three inches of the thread above the cork; it was then pushed down until the quicksilver was only just visible above the cork, and the reading noted; it was then pulled up again, and readings taken in various positions, as given in the following table; finally the thermometer was again pushed down as far as possible, and the reading taken, when it was found to be the same as before, showing that no change in the 100°-point had supervened during the experiment. Of several series of observations made in this manner, the one contained in the following table will suffice, since they all led to precisely the same result.

Reading of Standard when wholly immersed = 393·42.
Barometric pressure, corrected and reduced, = 760·1.
Corresponding temperature of steam = 100°·00.

Number of divisions surrounded by cold water and occupied by mercury.	Temperature of water.	Reading of Standard, T.	Value of C = 393·42 − T.	Value of m, $= \frac{C}{(T-t)N}$
317	13°·0	389·01	4·41	·0001599
277·5	12·3	389·54	3·88	·0001594
221	12·0	390·30	3·12	·0001604
173	12·1	390·94	2·48	·0001631
130	12·1	391·58	1·84	·0001610
79	12·1	392·30	1·12	·0001612

An inspection of the above table is sufficient to convince us that the value of m is constant, and equal to the apparent expansion of mercury in the glass of which the thermometer was made; the numbers would probably have agreed even more closely, were it not that it is impossible to arrange the apparatus so that the cold portion of the thermometer-stem follows directly upon the hot portion. There must always be an interval occupied by the cork, the temperature of which is uncertain. It should be remarked that there is no indication whatever of the value of m increasing when that of N increases.

Precisely the same results were obtained with the second standard thermometer, as is shown by the following table:—

Reading of Standard BS, when wholly immersed, = 419·21.
Barometric pressure, corrected and reduced, = 760·5.
Corresponding temperature of steam = 100°·02.

Number of divisions surrounded by cold water and occupied by mercury.	Temperature of water.	Reading of Standard BS, = T.	Value of C, = 419·21 − T.	Value of m, $= \frac{C}{(T-t)N}$
302	12°·0	415·13	4·08	·0001535
237	11·9	415·96	3·25	·0001556
174	12·0	416·84	2·37	·0001548
127	12·0	417·47	1·74	·0001557

Here, again, the value of m varies only within the limits of the error of observation, and shows no tendency to increase

when N increases. It may be noted that with both the above thermometers the mean value of m is *greater* than ·0001545, the value usually assigned to it, but that it differs from that number by so little that the error committed by substituting the one for the other in the calculation of the correction C will rarely amount to more than 0°·02 C.

The above experiments were made at 100°, because this is the only temperature which can be maintained absolutely constant for an hour without the use of a quantity of complicated apparatus; and it is evident that the slightest variation in the temperature would entirely spoil the series of observations. At higher temperatures the sources of error which beset the readings of thermometers increase so rapidly that the exact value of the coefficient m becomes of less and less importance as the temperature rises, notwithstanding the fact that the correction C increases in amount. Since there is no reason whatever to suppose that any different results would be obtained at such higher temperatures, I thought it unnecessary to make any further experiments, more especially as those given above yielded precisely those numbers which the ordinary laws of expansion predicted.

There is another point connected with thermometry, to which I devoted attention some years ago. It has been suggested that when a thermometer is placed in a vapour at maximum tension, as in the ordinary chemical process of distillation, it does not truly indicate the temperature of the vapour. This suggestion owes its origin to the fact that drops are seen to accumulate and drop off the end of the thermometer. It has been supposed that this condensation of the vapour on a surface which should be as hot itself, is due to the molecular attraction of the glass for the vapour. If this be the case, the heat evolved by the vapour during liquefaction on the thermometer-bulb would raise the temperature of the latter. The thermometer would thus indicate a higher temperature than that of the mass of the vapour. The experiments which I made upon this subject, like those instituted by others, were inconclusive. I possess, however, an apparatus which seems to me eminently suited to answer the question satisfactorily. It is at present being employed for other purposes; but I trust that, when it is at liberty, I shall be able to put it to this not unimportant use.

XV. *On the Determination of Chemical Affinity in terms of Electromotive Force.*—Part VI. *By* C. R. Alder Wright, *D.Sc. (Lond.), F.R.S., Lecturer on Chemistry and Physics in St. Mary's Hospital Medical School*.*

On the Relations between the Electromotive Forces of various kinds of Cells analogous to Daniell's Cell but differing therefrom in the nature of the Metals used, and the Chemical Affinities involved in the Action of these Cells.

I. *Cells containing Cadmium as one of the Metals, the Salts used being Sulphates.*

118. The experiments described in Part V. (§§ 106–109) were repeated, using, instead of normal Daniell cells, analogous arrangements containing plates of cadmium, opposed in some instances to copper, in others to zinc, solutions of the respective sulphates being employed to surround the various plates used. With each of these two classes of cells (cadmium-copper and zinc-cadmium cells) the same result was obtained as that already recorded in the case of Daniell cells containing zinc- and copper-sulphate solutions—viz. that so long as the two solutions are of the same strength† the actual state of concentration of the fluids does not exert any appreciable influence on the E.M.F. generated with given plate-surfaces; at least the influence exerted is considerably less than the errors of observation and the variations

* Read June 24, 1882.

† It is convenient to define solutions "of the same strength" not as solutions of the kind usually spoken of by chemists as "equivalent" to one another, *i. e.* containing in a given volume quantities of dissolved matter in the ratio of the chemical equivalents of the substances dissolved (*e. g.* 159·5, 161, and 208 parts of anhydrous copper, zinc, and cadmium sulphate respectively), but as solutions in which *the dissolved matter and the water present are in the same molecular ratio*, i. e. which are expressible by parallel formulæ, such as $CuSO_4\,50H_2O$, $ZnSO_4\,50H_2O$, and $CdSO_4\,50H_2O$. With weak solutions the two definitions are practically the same—but not so with more concentrated fluids, especially when the molecular weights of the dissolved matters are considerably different (like $CuSO_4$ and $CdSO_4$). Solutions of zinc and copper sulphate of the same molecular strength are practically identical in specific gravity; but a solution of cadmium sulphate is considerably more dense than one of either zinc or copper sulphate of the same molecular strength. Thus solutions of the strengths $ZnSO_4\,50H_2O$, $CuSO_4\,50H_2O$, $CdSO_4\,50H_2O$ have at 18° specific gravities respectively close to 1·170, 1·167, and 1·208; with stronger solutions the excess of density of the cadmium solution is still more apparent.

due to unavoidable variations in the nature of the plate-surfaces, and does not amount to as much as $\pm$·0015 volt even when tolerably concentrated solutions of strength $MSO_4\ 50H_2O$ are compared with similar solutions of only one twenty-fifth the strength, $MSO_4\ 1250\,H_2O$.

On varying the nature of the surface of the cadmium plate (by employing bright cast metal, electro-deposited cadmium, or amalgamated cadmium), it was found that whatever result was produced in the cadmium-copper cells by a given alteration of the cadmium plate, every thing else remaining unaltered, *precisely the same numerical result, but with the opposite sign, was produced in the zinc-cadmium cells* by that alteration. Thus, substituting electro-cadmium for bright cadmium plates in the cadmium-copper cells caused an *increase* in the E.M.F. varying from ·002 to ·006 volt in numerous experiments, and averaging ·004 volt; whilst with the zinc-cadmium cells the same substitution caused a *decrease* in the E.M.F. varying between almost the same limits, ·002 and ·007 volt, and averaging almost the same value as before, viz. ·0045 volt. Similarly, on substituting amalgamated cadmium plates for bright cadmium in the cadmium-copper cells, the average effect was a *decrease* of ·0415 volt when the mercurial amalgam was fluid, and of ·015 volt when it had become solid and crystalline on standing; whilst with the zinc-cadmium cells, substitution for bright cadmium of amalgamated metal caused on an average an *increase* in E.M.F. of ·043 volt when the amalgam was fluid, and of ·016 volt when it had become solid and crystalline.

Cells containing Cadmium opposed to Copper.

119. On comparing together a number of similar pairs of cells containing in the one case electro-copper and in the other amalgamated copper, it was found that the average difference was sensibly the same as that observed when the same two kinds of copper plates were opposed to zinc (§ 107), viz. that, *cæteris paribus*, the cell containing amalgamated copper read on an average ·001 volt lower than the one containing freshly deposited electro-copper: the actually observed differences ranged from +·003 to −·003 volt, but were more usually negative.

As just stated, when the cadmium plate was amalgamated a decrease in E.M.F. was brought about, averaging ·0415 volt when the amalgam on the surface of the plate was fresh and

perfectly fluid, and ·015 when perfectly solid and crystalline. Intermediate numbers were given by plates on the surface of which crystallization of the amalgam had begun but was not complete, the gradation being regular as the crystallization progressed.

The following table gives the average result, in volts*, of upwards of forty series of observations and comparisons, mostly extending over three to four hours, during which time the readings of each particular cell remained sensibly constant:—

Variation in E.M.F. due to the use of cadmium and copper sulphate solutions of different strengths, both solutions being of equal molecular strengths in any given case (strengths varying from $MSO_4\ 47\,H_2O$, to $MSO_4\ 1250\,H_2O$)† . . . . . } Less than ±·0015.

	Maximum.	Minimum.	Range.	Average.
Effect of substituting for electro-copper:—				
Amalgamated copper (surface wet with liquid mercury)	+·003	−·003	·006	−·001
Effect of substituting for bright cadmium:—				
Fresh electro-cadmium	+·006	+·002	·004	+·004
Amalgamated cadmium (surface wet with liquid mercury)	−·050	−·033	·017	−·0415
Amalgamated cadmium (solid and crystalline)	−·020	−·005	·015	−·015
Electromotive force of combinations:—				
Electro-copper—Electro-cadmium	·756	·750	·006	·7525
„ „ Bright cadmium	·753	·745	·008	·7485
„ „ Amalgamated cadmium (liquid amalgam)	·717	·701	·016	·707
„ „ Amalgamated cadmium (solid amalgam)	·740	·727	·013	7335
Amalgamated copper—Electro-cadmium	·754	·749	·005	·7515
„ „ Bright cadmium	·752	·744	·008	·7475
„ „ Amalgamated cadmium (liquid amalgam)	·715	·701	·014	·706
„ „ Amalgamated cadmium (solid amalgam)	·737	·727	·010	·7325

* All the observations given in this paper are reduced to the same standard as that employed in Part V.—viz. the average reading at 15°·5 of a number of Clark's cells taken as 1·457 volt, the particular Clark's cells used being the same throughout.

† The specific gravities at about 19° of these fluids are close to the following:—

$MSO_4\ 47\,H_2O$ when M is cadmium: spec. grav. = 1·217.
do. when M is copper: spec. grav. = 1·175; solution nearly saturated.
$MSO_4\ 1250\,H_2O$: in each case below 1·01.

When cells containing bright or electro-cadmium and electro-copper plates were allowed to stand for twelve hours or longer periods, a slight alteration in the E.M.F., due to formation of films of oxide on the surfaces of the plates, was usually noticeable. As with the normal Daniells (§ 108), the effect of the oxidation of the copper plate was to reduce the E.M.F. by a few thousandths of a volt; on the other hand, the formation of a film of oxide on the surface of the cadmium plate produced an *increase* in the E.M.F. of from ·001 to ·004 volt; so that in many cases the cell with partially oxidized plates gave sensibly the same value as a newly set-up cell, the diminishing effect of the oxidation of the copper being just about counterbalanced by the increasing effect due to the oxidation of the cadmium. In this respect cadmium behaves in the opposite way to zinc (§ 108).

Relations between the E.M.F. of Cadmium-Copper Cells and that corresponding to the net Chemical Action taking place therein.

120. According to Julius Thomsen's determinations (*Journ. prak. Chem.* ii. p. 233, and xi. p. 271), the heat of displacement of copper from copper-sulphate solution ($CuSO_4$,400H_2O) by cadmium is as follows, in gramme-degrees per gramme-molecule:—

Cd, O, SO_3 aq. . . .	89,500
Cu, O, SO_3 aq. . . .	55,960
Difference =	33,540

the difference corresponding to 16,770 gramme-degrees per gramme equivalent, or ·740 volt*. As with normal Daniell cells (§ 114), a small quantity (x) is to be added to this, representing a variable correction dependent on the physical condition of the deposited copper. Evidently the average values above cited (·7475 to ·7525), obtained with bright and electro-cadmium, are sensibly the same as the value ·740 + x, thus deduced as representing the net chemical action taking place in the cell; *i. e.*, as with zinc-copper cells, the whole of the

* The value 4410, used in the former parts of these researches for the factor for converting gramme-degrees into C.G.S. units, is employed throughout the present paper; *vide* § 103, footnote.

energy developed in the cell is adjuvant under the conditions obtaining in the above experiments.

In order to compare the results obtained with the amalgamated-cadmium cells with Julius Thomsen's figures, the heat of solution of cadmium (precipitated from the sulphate by zinc, crystalline) in twenty-five times its weight of mercury was determined by means of the calorimeter, 20 grams of cadmium and 500 of pure mercury being employed for each experiment. To insure solution it was found necessary to wash the cadmium with dilute sulphuric acid just before use; otherwise portions remained unwetted and undissolved by the mercury. The final result arrived at as the average of several concordant observations was, that an evolution of heat to the extent of 610 gramme-degrees per gramme-molecule (112 grammes) of cadmium took place during solution. Hence, were cadmium sulphate formed from mercurial solution of metal instead of crystalline precipitated metal, the heat of formation expressed as Cd, O, SO_3 aq. would be $89{,}500 - 610 = 88{,}890$ (admitting that Thomsen's value 89,500 applies, without correction, to the metal in the crystalline condition of that experimented with). Consequently the heat of displacement of copper by cadmium from the sulphate is 32,930 per gramme-molecule, or 16,465 per gramme-equivalent, corresponding to ·726 volt. The observed values varied between ·701 and ·717, averaging ·707 with electro-copper and ·706 with amalgamated copper—again not differing from the value deduced from the thermal data by an amount materially outside the limits of experimental errors, especially those due to variation in the heat of formation of salts according as the physical state of the metal employed varies.

It is, however, to be noticed that the above heat of solution of crystalline cadmium in mercury only corresponds to an E.M.F. of ·0135 volt; whilst the average difference in E.M.F. caused by the substitution of fluid amalgamated cadmium for crystalline electro-metal was $·7525 - ·707 = ·0455$ volt, a considerably greater amount; so that amalgamating the crystalline metal appears to produce a greater effect on the E.M.F. than corresponds to the heat of solution. Just the same result is produced when cadmium and zinc are opposed (§ 121); on the other hand, the effect on the E.M.F. of amalgamating silver

is sensibly the same as that corresponding to the heat of solution of silver in mercury (§ 129). Probably the difference in the cases of silver and cadmium is due to the oxidizability of the latter by dissolved air, thus rendering the outer surface of the crystalline masses somewhat different from the interior.

Cells containing Cadmium opposed to Zinc.

121. The following table exhibits in brief the results of upwards of thirty series of observations, mostly lasting over several hours, during which period the E.M.F. developed by any given cell remained sensibly steady :—

Variation in E.M.F. due to the use of cadmium and zinc sulphate solutions of different strengths, both solutions being of equal molecular strengths in any given case (strengths varying from $MSO_4 50H_2O$ to $MSO_4 1250H_2O$)	Less than $\pm$·0015 volt.

	Maximum.	Minimum.	Range.	Average.
Effect of substituting for bright cadmium :—				
Fresh electro-metal	−·002	−·007	·005	−·0045
Amalgamated cadmium (liquid)	+·052	+·036	·016	+·044
„ „ (solid, crystalline)	+·024	+·009	·015	+·0165
Electromotive force of combinations:—				
Amalgamated zinc—Bright cadmium	·367	·361	·006	·364
„ „ Electro-cadmium	·362	·358	·004	·360
„ „ Amalgamated cadmium (liquid)	·414	·401	·013	·4075
„ „ Amalgamated cadmium (solid)	·388	·373	·015	·3805

These figures accord closely with the results deducible from Julius Thomsen's thermochemical data, together with the heat of solution of cadmium in mercury above quoted (§ 120); thus:—

	Free metallic cadmium.	Cadmium dissolved in mercury.
Zn, O, SO_3 aq. . . .	=106090	106090
Cd, O, SO_3 aq. . . .	= 89500	88890
Difference . .	16590	17200
Difference per gramme-equivalent . . .	8295	8600
Corresponding with volt	·365	·379

The observed electromotive forces* thus do not differ from those corresponding with the thermal values by amounts materially outside the experimental errors. As with the copper-cadmium cells, however, the observed difference in E.M.F. between electro-cadmium (crystalline) and amalgamated cadmium (liquid) is notably greater than that corresponding with the heat of solution of precipitated crystalline cadmium in mercury, being ·407 − ·3595 = ·0475 as compared with ·0135 volt.

Volta's Law of Summation of Electromotive Forces.

122. The foregoing experiments clearly show that, as far as cells containing zinc, cadmium, and copper plates are concerned, Volta's law of summation holds, at any rate when the plates are immersed in solutions of their respective sulphates, the solutions being of equal molecular strength; that is, the sum of the electromotive forces generated with a given pair of zinc and cadmium plates, and with that same cadmium plate and a given copper plate, is equal to the E.M.F. generated with the given zinc and copper plates; or, otherwise,

$$\left\{\begin{matrix}\mathrm{Zn}\\ \mathrm{Cd}\end{matrix}\right. + \left\{\begin{matrix}\mathrm{Cd}\\ \mathrm{Cu}\end{matrix}\right. = \left\{\begin{matrix}\mathrm{Zn}\\ \mathrm{Cu}\end{matrix}\right.$$

where the symbol $\left\{\begin{matrix}\mathrm{Zn}\\ \mathrm{Cd}\end{matrix}\right.$ represents the E.M.F. generated with a given kind of zinc plate opposed to a given kind of cadmium plate, each plate being immersed in a solution of its sulphate of constant molecular strength.

* Regnault has shown (*Ann. de Chim. et de Phys.* [3] xliv. p. 453) that the E.M.F. of a cell containing "concentrated" solutions of zinc and cadmium sulphates and plates of these metals was 55, when that of a similar cell with zinc and copper sulphates and plates was 175 (a particular thermopile being employed as unit). Taking the E.M.F. of the latter cell as 1·115 volt, that of the former must have been ·350 volt—a value differing from those observed by an amount not outside that possibly due to inequality in the molecular strengths of the two metallic solutions. For, by the use of more dilute cadmium-sulphate solutions (the zinc-sulphate solution remaining the same) an appreciable fall in E.M.F. was found to be produced, the lowest value being 42 = ·268 volt with solution diluted to $\frac{1}{100}$; on the other hand, decreasing the strength of the zinc-sulphate solution produced far less effect. These and the author's somewhat different results on this point will be discussed in a future paper.

Thus the average results for Daniell cells quoted in Part V. and the above figures give the following comparisons:—

Nature of Plate-surfaces.			Electromotive Force developed.			Normal Daniell.
Zinc.	Cadmium.	Copper.	Zinc-Cadmium.	Cadmium-copper.	Sum.	
Amalgamated.	Electro.	Electro.	·3595	·7525	1·112	Amalgamated zinc and electro-copper 1·111 to 1·116, averaging 1·114.
,,	Bright.	,,	·364	·7485	1·1125	
,,	Amalgamated (fluid).	,,	·407	·707	1·114	
,,	Amalgamated (solid).	,,	·380	·7335	1·1135	
				Mean ...	1·1130	
Amalgamated.	Electro.	Amalgamated.	·3595	·7515	1·111	Amalgamated zinc and amalgamated copper 1·110 to 1·115, averaging 1·113.
,,	Bright.	,,	·364	·7475	1·1115	
,,	Amalgamated (fluid).	,,	·407	·706	1·113	
,,	Amalgamated (solid).	,,	·380	·7325	1·1125	
				Mean ...	1·1120	

A number of direct experiments were also made on this point, using *twin cells* constructed as follows:—Three beakers were arranged containing solutions of copper, cadmium, and zinc sulphates of the same molecular strengths, and plates of electro-copper, bright (or electro-) cadmium, and amalgamated zinc respectively. The copper and cadmium beakers were connected by a siphon tube (with ends covered with bladder) filled with the cadmium sulphate solution; and the cadmium and zinc beakers were similarly connected by a siphon tube containing the zinc sulphate solution. The copper, cadmium, and zinc plates were then connected with cups Nos. 1, 2, and 3 respectively of a switch-board like that represented in fig. 3, Part V. (§ 106); so that by connecting cups 1 and 2 with the electrometer the E.M.F. of the cadmium-copper cell was determined, whilst when cups 2 and 3 were connected the E.M.F. of the cadmium-zinc combination was determined. These readings having been made several times, the zinc and copper plates were transferred to another pair of beakers, containing the same zinc and copper sulphate solutions united by a zinc-sulphate siphon, so as to constitute a

normal Daniell cell after Raoult's pattern, and the E.M.F. of this combination determined. Several pairs of zinc and copper plates were thus used—each pair being read first in the zinc-cadmium-copper combination, then in the normal Daniell cell, and then again in the ternary combination. In each case the difference between the sum of the average electromotive forces of the zinc-cadmium and cadmium-copper couples differed from that of the zinc-copper combination by quantities no greater than the errors of observation of the electrometer-scale (about $\pm 0{\cdot}1$ per cent. when a sufficient number of readings were taken); whilst the average of the small differences observed with different pairs was actually 0, *the small + and − differences due to errors of observation completely balancing one another.* This final result (that no discernible difference was to be found between the sum of zinc-cadmium and cadmium-copper couples, and zinc-copper couples containing the same plates) was obtained in each of several sets of experiments made respectively with solutions of molecular strength $MSO_4\,47\,H_2O$, $MSO_4\,100\,H_2O$, and $MSO_4\,1250\,H_2O$.

Rate of Fall in E.M.F. through so-called Polarization occurring in Zinc-Cadmium and Cadmium-Copper Cells for definite amounts of Increase in the Rates of Current-flow.

123. The experiments made with normal Daniell cells described in Part V. (§§ 103–105) were repeated with zinc-cadmium and with cadmium-copper plates (exposing surfaces of $2{\cdot}5$ and $5{\cdot}0$ square centimetres). The results were similar in character to those obtained with the Daniell cells, no appreciable falling-off in E.M.F. occurring with a current-density of less than some 5 to 10 microampères per square centimetre of plate-surface, but very considerable amounts being observed with stronger currents.

Thus the following table exhibits the values obtained in four experiments—the first three with zinc-cadmium plates, the fourth with cadmium-copper plates, solutions of sulphates of the respective metals employed being used throughout:—

Zinc plates ..... / Cadmium plates ... / Copper plates	Amalgamated. / Electro /	Amalgamated. / Amalgamated. / Fluid amalgam. /	Amalgamated. / Amalgamated. / Solid amalgam. /	..... / Bright. / Electro.
Sp. gr. of zinc sulphate solution...	1·17	1·17	1·17	.....
Sp. gr. of cadmium sulphate solution	1·25	1·32	1·32	1·32
Sp. gr. of copper sulphate solution	.....	.....	.....	1·17
Resistance of cell, in ohms	9·5	10·5	11·0	7·4
Maximum E.M.F., in volts	·366	·418	·395	·741
Current-density, in microampères per square centimetre.	Observed amounts of Fall in E.M.F.			
10	0	0	0	·001
20	0	·001	·001	·004
40	·001	·002	·003	·008
100	·002	·004	·007	·014
200	·004	·007	·011	·020
400	·012	·013	·017	·030
1000	·026	·030	·030	·049
2000	·049	·059	·055	·077
4000	·088	·099	·094	·128

The values are represented graphically by the curves marked I., II., III., and IV. respectively in the annexed figure.

A number of experiments were made with cells containing solutions not of equal molecular strengths (like those described in § 110), for the purpose of finding how much of the diminutions observed with the larger current-densities might possibly be due to the strengthening of the solution round the dissolved plate, and the weakening of the liquid round the other plate, which takes place whilst the cell is in action. The general result was that the maximum possible diminution due to these causes could not exceed about ·04 volt. The details of these experiments and of others allied thereto will be discussed in a future paper.

Effect of varying the Size of one of the Plates, the other remaining constant.

124. The experiments described in Part V. (§ 115) were repeated with various cells containing copper-cadmium or zinc-cadmium plates instead of zinc-copper ones. The following values obtained in four such experiments illustrate the results obtained, indicating that the effect of halving the area of the plate on which metal is deposited is, as with the Daniell cells, greater than the effect of halving the area of the dissolved plate, when the former plate is not mercurialized*. The zinc-cadmium cells, however, differ from ordinary Daniell cells in this respect—that, whilst amalgamating the copper plate of a Daniell cell does not materially alter the relative effect of halving its area, amalgamating the cadmium plate of a zinc-cadmium cell greatly diminishes the relative effect of halving its area, in such sort that, when solid crystalline amalgam is used, the effect of halving the area of the cadmium plates, instead of exceeding, becomes sensibly equal to the effect of halving the area of the zinc plate, whilst when liquid amalgam is used the effect of halving the area of the cadmium plate becomes sensibly less than the effect of halving that of the zinc plate.

* It is noteworthy in this connexion, that when nearly pure wrought-iron plates, immersed in ferrous sulphate solution, replace the zinc plates and zinc sulphate solution of normal Daniell cells, the effect of halving the area of the iron plates sometimes *exceeds* that produced by halving the area of the copper plates

Current, in micro-ampères.	Cadmium-Copper.		Zinc-Cadmium.					
	Bright cadmium—Electro-copper.		Amalgamated zinc—Electro-cadmium.		Amalgamated zinc—Fluid amalgamated cadmium.		Amalgamated zinc—Solid amalgamated cadmium.	
	Effect of halving area of		Effect of halving area of		Effect of halving area of		Effect of halving area of	
	Cadmium.	Copper.	Zinc.	Cadmium.	Zinc.	Cadmium.	Zinc.	Cadmium.
1000	·005	·008	·004	·005	·005	·003	·005	·006
2000	·010	·013	·007	·008	·009	·005	·011	·015
5000	·016	·022	·012	·013	·018	·011	·021	·019
10000	·020	·031	·020	·025	·027	·015	·026	·025
20000	·039	·051	·030	·040	·035	·022	·032	·032

II. *Cells containing Silver as one of the Metals, the Salts used being Sulphates.*

125. Three sets of cells, after Raoult's pattern, were constructed, containing respectively zinc-silver, cadmium-silver, and copper-silver couples, the respective plates being immersed in solutions of silver sulphate saturated at ordinary temperatures, and of copper and zinc sulphate of strengths molecularly equal thereto (the silver solution contained 7·25 grammes of Ag_2SO_4 per litre, and had a sp. gr. near to 1·0067); the composition was uniformly $MSO_4\,2360\,H_2O$.

On making series of determinations of the E.M.F.'s of these cells, the following results were arrived at as the effects of varying the nature of the silver surfaces, deduced from the average values of a large number of observations (upwards of 50 sets of comparisons).

Effect of substituting Electro-Silver for Bright Silver.

	Zinc opposed.	Cadmium opposed.	Copper opposed.
Maximum ...	+·017	+·015	+·012
Minimum ...	+·003	+·005	+·004
Range.....	·014	·010	·008
Average.....	+·008	+·009	+·0075

Effect of substituting Amalgamated Silver (fluid) for Bright Silver.

Maximum ...	+·102	+·110	+·105
Minimum ...	+·092	+·095	+·092
Range.....	·010	·015	·013
Average.....	+·099	+·101	+·1025

Considering the perceptibly wider ranges of variation in these experiments than those usually observed in the zinc-cadmium-copper cells previously described, it is evident that the effect of varying the nature of the silver plate is sensibly independent of the nature of the other metal.

Sometimes, but not invariably, the amalgamated silver plates became solid and crystalline (greenish yellow) on the surface: this result was apparently brought about much more rapidly when the silver was immersed in concentrated zinc sulphate solution than under any other of the conditions obtaining in the various experiments. When this change took place the E.M.F. set up by opposing such a plate to zinc in cells containing sulphates of zinc and silver was always intermediate between that set up in the same fluids by plates of bright silver and of fluid amalgamated silver. The average of several comparisons was as follows:—

Effect of substituting Amalgamated Silver (solid) for Bright Silver.

Maximum.....	+·025
Minimum.....	+·014
Range	·011
Average	+·021

In this respect silver is analogous to cadmium when the latter is opposed to zinc (§ 121); but the average amounts of increase in E.M.F. due to fluid and solid amalgam are in each instance considerably greater with silver than with cadmium (·099 and ·021 for silver as compared with ·043 and ·016 for cadmium).

On substituting electro- for bright cadmium in the cadmium-silver cells, identically the same average effect was observed as in the cadmium-copper cells (§ 119), viz. an increase in the E.M.F. of from ·002 to ·006, averaging ·004 volt. Similarly, on

substituting amalgamated for electro-copper in the copper-silver cells, practically the same numerical difference in the E.M.F. was brought about as was formerly observed in the zinc-copper cells (§ 107) and the cadmium-copper cells (§ 119), but in the opposite direction, the E.M.F. being *raised* in the copper-silver cells and lowered in the other two kinds: the alteration in the E.M.F. varied between +·005 and −·003, averaging +·0005.

126. On allowing newly set-up cells to stand for several hours, different results were brought about in each of the three cases according as the silver was opposed to zinc, cadmium, or copper. In the first case the E.M.F. invariably fell; the maximum value was observed immediately after the cell was set up, and continued sensibly steady for a variable period of time, a distinct diminution becoming perceptible sometimes after half an hour, sometimes only after two or three hours. With cadmium the value after several hours was somewhat greater than that set up at first and during the subsequent hour or so; and with copper the value attained after several hours was still greater than that exhibited during the first hour or two. The following numbers represent the average alterations thus observed, being the differences between the average readings during the first hour and during a period of from 3 to 5 hours after setting up :—

Amalgamated Zinc opposed.

Bright silver.	Electro-silver.	Amalgamated silver.	Mean.
−·010	−·014	−·012	−·012

Bright Cadmium opposed.

+·003	+·001	+·003	+·002

Electro-Cadmium opposed.

+·003	+·004	+·003	+·003

Electro-Copper opposed.

+·009	+·007	+·007	+·008

Amalgamated Copper opposed.

+·011	+·009	+·005	+·008

These alterations were traced to the variations in the nature of the surfaces of the plates opposed to the silver; for on

taking out, for instance, an amalgamated zinc plate after 5 hours, and replacing by a freshly amalgamated plate, the E.M.F. was restored to sensibly the same value as at first; and similarly with the other metals. On the other hand, on taking out from two cells, for instance, a zinc and a copper plate after 5 hours, and replacing them respectively in two beakers containing zinc and copper sulphate solutions of the same molecular strengths, and connected by a siphon tube, the E.M.F. of the cell thus formed was found to fall short of the average value of a normal Daniell cell with fresh plates by an amount sensibly equal to the sum of the numerical alterations that had occurred in the zinc-silver and copper-silver cells jointly. It is specially noticeable that, whilst in zinc-copper cells the alteration in the surface of the copper (probably through oxidation) on standing diminishes the E.M.F., in copper-silver cells the alteration is in the opposite direction: with zinc and cadmium the direction of this alteration when opposed to silver is the same as when opposed to copper.

It would seem from all these results that the effect of a given alteration of the surface of one of the plates of a voltaic pair upon the E.M.F. of the pair is independent of the nature of the other plate as regards its numerical value, although the nature of this second plate regulates the direction of the variation in the E.M.F. produced (increase or decrease), and also exerts an influence upon the rate at which the alteration of the plate-surface takes place. Thus it was repeatedly observed that, whereas an amalgamated zinc plate (or an electro-copper one), when forming part of a normal Daniell cell, did not become sensibly oxidized, so as to diminish the E.M.F. of the cell, until after several hours at least had elapsed, a precisely similar plate immersed in the same liquid, but forming part of a zinc-silver cell (or of a copper-silver cell), did become perceptibly oxidized in much less time. In other words, although no measurable current was generated in either case, yet the different amounts of strain (so to speak) set up in the chain of liquid particles between the two plates, according as one was silver or not, did affect the rate of change in the surface of the more oxidizable metal (presumably by varying the rate at which it combined with the oxygen dissolved in the fluid).

127. The following Table exhibits the average results obtained in about 150 sets of observations and comparisons, only those values made during the first hour (or sometimes less) after setting up being taken into account, and all subsequent values being rejected where any diminution through oxidation &c. began to be perceptible *. The values cited as the average effects of substituting for bright silver electro- and amalgamated (liquid) silver are the means of the three sets above quoted (§ 125) obtained respectively with zinc, cadmium, and copper :—

	Maximum.	Minimum.	Range.	Average.
Effect of substituting for bright silver :—				
Electro-silver	+·017	+·003	·014	+·008
Amalgamated silver (liquid)	+·100	+·092	·008	+·101
„ „ (solid)	+·025	+·014	·011	+·021
Effect of substituting for electro-copper :—				
Amalgamated copper	+·005	−·003	·008	+·001
Effect of substituting for bright cadmium :—				
Electro-cadmium	+·006	+·002	·004	+·004
Electromotive force of combinations :—				
Amalgamated zinc—Bright silver	1·540	1·518	·022	1·528
„ „ Electro-silver	1·550	1·529	·021	1·536
„ „ Amalg.silver(liquid)	1·640	1·615	·025	1·627
„ „ „ „ (solid).	1·555	1·544	·011	1·549
Bright cadmium—Bright silver	1·173	1·163	·010	1·1675
„ „ Electro-silver	1·185	1·169	·016	1·1765
„ „ Amalg. silver (liquid).	1·278	1·261	·017	1·2685
Electro-cadmium—Bright silver	1·176	1·164	·012	1·1715
„ „ Electro-silver	1·186	1·176	·010	1·1805
„ „ Amalg. silver (liquid)	1·277	1·267	·010	1·2725
Electro-copper—Bright silver	·422	·411	·011	·416
„ „ Electro-silver	·429	·411	·018	·4235
„ „ Amalg. silver (liquid)...	·535	·513	·022	·5185
Amalgamated copper—Bright silver	·420	·411	·009	·4165
„ „ Electro-silver	·430	·414	·016	.424
„ „ Amalg. silver (liquid)	·535	·513	·022	·519

Volta's Law of Summation.

128. The values in this table, together with those quoted above for the zinc-cadmium and cadmium-copper cells (§§

* Notwithstanding all care, it is probable that the average results with the zinc-silver cells are too low by a few thousandths of a volt, and those with the other cells slightly too high (vide § 128).

119 and 121) and those given in Part V. for zinc-copper cells (§ 107), clearly prove that Volta's law holds in the case of the sets of combinations

$$\text{(A)} \quad \begin{Bmatrix} \text{Zn} \\ \text{Cd} \end{Bmatrix} + \begin{Bmatrix} \text{Cd} \\ \text{Ag} \end{Bmatrix} = \begin{Bmatrix} \text{Zn} \\ \text{Ag} \end{Bmatrix}$$

$$\text{(B)} \quad \begin{Bmatrix} \text{Zn} \\ \text{Cu} \end{Bmatrix} + \begin{Bmatrix} \text{Cu} \\ \text{Ag} \end{Bmatrix} = \begin{Bmatrix} \text{Zn} \\ \text{Ag} \end{Bmatrix}$$

$$\text{(C)} \quad \begin{Bmatrix} \text{Cd} \\ \text{Cu} \end{Bmatrix} + \begin{Bmatrix} \text{Cu} \\ \text{Ag} \end{Bmatrix} = \begin{Bmatrix} \text{Cd} \\ \text{Ag} \end{Bmatrix}$$

at any rate within the range of possible error due to the somewhat larger ranges of fluctuation in the E.M.F. of silver-containing cells than were observed with zinc-cadmium-copper cells, and to the fact that, although alterations of the oxidizable plates in the cells containing silver was avoided as far as possible by only carrying on the observations for one hour and sometimes less, still it was not practicable wholly to avoid this source of inaccuracy. Thus in the three cases respectively the following figures are obtained (see pages 148, 149).

Average difference in case	A	=	+·0042
„ „ „	B	=	+·0027
„ „ „	C	=	−·0032
	Mean.....	=	+·0012

On carrying out twin-cell experiments like those described in § 122, it was found that when a silver plate was placed in the central beaker, and either copper and zinc, copper and cadmium, or zinc and cadmium plates were used in the other beakers, together with solutions of the respective metallic sulphates of the same molecular strengths, the difference between the electromotive forces determined in the twin cell was always sensibly equal to the E.M.F. developed by the pair of plates other than silver employed when taken out and opposed to each other in an ordinary cell containing the same metallic solutions; and this was found to be the case, not only with freshly-prepared plates, but also with plates that had been immersed for hours and had become oxidized on the surface.

Case A.

Nature of Plate-surfaces.			Electromotive Forces developed.				
Zinc.	Cadmium.	Silver.	Zinc-cadmium.	Cadmium-silver.	Sum.	Zinc-silver.	Difference.
Amalgamated.	Bright.	Bright.	·364	1·1675	1·5315	1·528	+·0035
,,	Electro.	,,	·3595	1·1715	1·531		+·003
,,	Bright.	Electro.	·364	1·1765	1·5405	1·536	+·0045
,,	Electro.	,,	·3595	1·1805	1·540		+·004
,,	Bright.	Amalgamated (liquid).	·364	1·2685	1·6325	1·627	+·0055
,,	Electro.	,,	·3595	1·2725	1·632		+·005

Average difference = +·0042

Case B.

Zinc.	Copper.	Silver.	Zinc-copper.	Copper-silver.	Sum.	Zinc-silver.	Difference.
Amalgamated.	Electro.	Bright.	1·114	·416	1·530	1·528	+·002
,,	Amalgamated.	,,	1·113	·4165	1·5295		+·0015
,,	Electro.	Electro.	1·114	·4235	1·5375	1·536	+·0015
,,	Amalgamated.	,,	1·113	·424	1·537		+·001
,,	Electro.	Amalgamated (liquid).	1·114	·5185	1·6325	1·627	+·0055
,,	Amalgamated.	,,	1·113	·519	1·632		+·005

Average difference = +·0027

Case C.

Nature of Plate-surfaces.			Electromotive Forces developed.				
Cadmium.	Copper.	Silver.	Cadmium-copper.	Copper-silver.	Sum.	Cadmium-silver.	Difference.
Bright.	Electro.	Bright.	·7485	·416	1·1645	1·1675	−·003
,,	Amalgamated.	,,	·7475	·4165	1·164		−·0035
,,	Electro.	Electro.	·7485	·4235	1·172	1·1765	−·0045
,,	Amalgamated.	,,	·7475	·424	1·1715		−·005
,,	Electro.	Amalgamated (liquid).	·7485	·5185	1·267	1·2685	−·0015
,,	Amalgamated.	,,	·7475	·519	1·2665		−·002
Electro.	Electro.	Bright.	·7525	·416	1·1685	1·1715	−·003
,,	Amalgamated.	,,	·7515	·4165	1·168		−·0035
,,	Electro.	Electro.	·7525	·4235	1·176	1·1805	−·0045
,,	Amalgamated.	,,	·7515	·424	1·1755		−·0050
,,	Electro.	Amalgamated (liquid).	·7525	·5185	1·271	1·2725	−·0015
,,	Amalgamated.	,,	·7515	·519	1·2705		−·0020

Average difference = −·0032

For instance, in a pair of experiments with amalgamated zinc, bright silver, and electro-copper plates:—

Cells newly set up.		After 24 hours.
Zinc-copper in single cell . .	1·115	1·098
Copper-silver in twin cell . .	·417	·425
Sum	1·532	1·523
Zinc-silver in twin cell . . .	1·534	1·522
Difference . .	−·002	+·001

Similar results were obtained in several other experiments of the same kind, both with zinc-copper plates opposed to silver and with the other two pairs (zinc-cadmium and cadmium-copper). The average difference in each case was considerably less than ±·001 volt.

Relations between the Electromotive Forces of Zinc-Silver, Copper-Silver, and Cadmium-Silver Cells and those corresponding to the net Chemical Actions taking place therein.

129. In all the cells hitherto examined in this series of researches there has been shown to be a sensible equality between the electromotive forces generated with clean plate-surfaces of pure metals and those corresponding to the net chemical and physical actions taking place therein. *A priori*, there does not seem to be any evident reason why the same state of things should not exist in the case of cells containing silver plates. Thomsen's thermo-chemical valuations, however, indicate that the electromotive forces corresponding to the three equations

$$Zn + Ag_2SO_4 = 2Ag + ZnSO_4,$$
$$Cd + Ag_2SO_4 = 2Ag + CdSO_4,$$
$$Cu + Ag_4SO_4 = 2Ag + CuSO_4,$$

are considerably higher than those actually observed and tabulated above, thus:—

Zinc-silver.		Cadmium-silver.		Copper-silve
Zn, O, SO_3 aq. =	106090	Cd, O, SO_3 aq. =	89500	Cu, O, SO_3 aq. = 5
Ag_2, O, SO_3 aq. =	20390	Ag_2, O, SO_3 aq. =	20390	Ag_2, O, SO_3 aq. = 2
Diff., per gramme-molecule	85700		69110	3
Diff., per gramme-equivalent.....	42850		34555	1
Corresponding to volt	1·890		1·524	

In each of the three cases the calculated E.M.F. is from ·34 to ·37 volt above the observed values when silver plates not amalgamated are used, indicating that even when only infinitesimal currents are generated a large amount of energy is nonadjuvant. It will be shown in a future paper that this behaviour is more or less marked in other kinds of cells containing silver plates and silver compounds, although the minimum amount of nonadjuvancy observed in any given case is variable with the nature of the saline compounds in the cell*. In order to see whether the rise in E.M.F. produced by amalgamating the silver plate is due simply to the heat of formation of silver sulphate being less when the silver is dissolved in mercury than when it is free, determinations of the heat of solution of silver (precipitated from the nitrate by copper, crystalline) were made. It was found a little difficult to get every trace of silver used dissolved in mercury when 20 grams of silver and 600 of mercury were employed, even though the surface of the former was washed with dilute nitric acid. With smaller amounts of mercury only incomplete solution was effected, more or less pasty amalgam being formed, and a smaller heat-development being then noticeable. The most trustworthy determinations made indicated that during the solution of 108 grams of silver, 2070 gramme-degrees are evolved. Hence the heat of formation of silver sulphate, when the silver is dissolved in mercury, is, per gramme-molecule, $20390 - 2 \times 2070 = 16250$; so that the heat of displacement of silver from silver sulphate, when the metal is ultimately obtained in mercurial solution, is greater than the values above calculated for zinc, cadmium, and copper respectively as precipitating metals by 4140 gramme-degrees per gramme-molecule, or 2070 per gramme-equivalent, corresponding with ·0915 volt. The average difference in E.M.F. between cells otherwise alike, in which crystalline electro-silver and amalgamated silver (fluid) are respectively used, is almost identical with this, being $\cdot 101 - \cdot 008 = \cdot 093$ volt. As already noticed (§ 120), silver and cadmium differ in their behaviour in this connexion

* Raoult has already obtained numbers (*Ann. Chim. et Phys.* [4] ii. 317 and iv. 392) indicating that the "galvanic heat" (§ 17) of a cell containing copper, silver, and the nitrates of their metals is sensibly below the value due to the net chemical action taking place. These and other similar observations will be discussed in a future paper.

when amalgamated, the inequality between the effect on the E.M.F. actually produced by amalgamation of cadmium and that corresponding with the heat of solution in mercury being probably due to the oxidation of cadmium by dissolved air.

Rate of Fall in Electromotive Force through so-called "Polarization" for definite Amount of Increase in Rate of Current-flow.

130. In order to see whether the electromotive forces of the cells above described are rendered less (when no current passes) than they otherwise would be, through the interfering action of dissolved air or some other similar obscure cause, a number of experiments were made like those described in Part V. (§§ 103–105), with the general result of showing that the deficiency observed in the E.M.F. actually generated when no current passes (as compared with that calculated from the thermo-chemical data) is at any rate not due to any such cause, inasmuch as the E.M.F. generated when a current does pass is always more or less *below* that set up when no current passes, just as with normal Daniell cells and with the zinc-cadmium and cadmium-copper cells above described. Thus, for example, the following numbers were obtained in three experiments, in each of which bright zinc plates were employed, and one in which electro-copper plates were used, the silver plates being in each instance uppermost and surrounded by saturated silver sulphate solution.

Fluid surrounding the zinc plates.	Zinc-sulphate solution, sp. gr. 1·42.	Zinc-sulphate solution, sp. gr. 1·42.	Zinc-sulphate solution, sp. gr. 1·10.	.....
Fluid surrounding the copper plates	.....	.....	.....	Copper sulphate sol., sp. gr. 1·17.
Nature of silver plates.	Electro-silver (crystalline.	Solid crystallized amalgam.	Solid crystallized amalgam.	Electro-silver (crystalline).
Resistance, in ohms, of column of fluid between plates	66·9	76·0	76·6	71·0
Maximum E.M.F.	1·500	1·511	1·546	·401

Current-density, in microampères.	Observed amounts of fall in Electromotive Force.			
20	.....	.....	·012	·005
50	·016	·010	·021	·011
100	·025	·018	·026	·019
200	·041	·036	·037	·030
400	·062	·067	·059	·047
600	·080	·097	·077	·063
1000	·116	·144	·112	
2000	·209	·258	·177	

These numbers are represented graphically by the curves marked respectively V., VI., VII., and VIII. in the figure.

On trying experiments, like those described in § 110, to see how far the falling-off in E.M.F. when a current is generated could be due to the accumulation of zinc (cadmium or copper) sulphate round the plate opposed to the silver, it was found that the maximum possible effect due to this cause could not exceed about ·04 volt with zinc and cadmium, and ·02 with copper. These experiments, and others of a similar nature, will be discussed in a future paper.

On comparing the eight curves represented in the figure with those previously described as obtained with various forms of Daniell cell (Part V. § 105), it is noticeable, first, that the curves obtained with the zinc-cadmium cells underlie all the others (I., II., and III.); secondly, that the curve with the cadmium-copper cell (IV.) is practically identical with one of the Daniell-cell curves—indicating consequently that, whilst the substitution of copper for cadmium in a zinc-cadmium cell raises the position of the curve (*i. e.* increases the rate of fall in E.M.F. according as the current-density increases), the substitution of cadmium for zinc in a Daniell cell does not materially alter the position of the curve; thirdly, the curves with the zinc-silver and copper-silver cells overlie all the others, whilst the copper-silver curve (VIII.) is not widely different from the zinc-silver curves (V., VI., and VII.)—indicating that, whilst the substitution of silver for copper in a Daniell cell largely raises the position of the curve, the effect of substituting copper for zinc in a zinc-silver cell is very much less marked. In other words, *the nature of the dissolved metal affects the rate of decrease in E.M.F. with increasing current-density much less than does the nature of the deposited metal; whilst the less the heat of formation of the salt of the latter that is decomposed by the passage of the current, the more rapid appears to be the rate of fall in the E.M.F. of the cell as the current-density increases.* As regards the first part of this general conclusion, it is precisely what also results from the majority of the previously described experiments on the effect of halving the area of the dissolved plate, as compared with that produced by halving the area of the plate on which metal is deposited. The following experiments with cells containing silver plates also give the same general results.

Effect of Varying the Size of one of the Plates in Cells containing Silver as one of the Metals, the other Plate remaining unaltered.

131. By operating in the way described in § 115, the following results were obtained in four sets of observations with zinc-silver and copper-silver cells, showing that, in all cases, halving the area of the silver plate produces a sensibly greater decrease in the E.M.F. set up with a constant rate of current-flow than is effected by halving the area of the plate opposed to the silver.

Current-density, in micro-ampères.	Zinc-Silver.						Copper-Silver.	
	Amalgamated zinc—electro-silver.		Amalgamated zinc—crystalline amalgamated silver.		Amalgamated zinc—crystalline amalgamated silver.		Electro-copper—electro-silver.	
	Effect of halving area of		Effect of halving area of		Effect of halving area of		Effect of halving area of	
	Zinc.	Silver.	Zinc.	Silver.	Zinc.	Silver.	Copper.	Silver.
1000	·009	·011	·007	·026	·008	·019	·004	·011
2000	·012	·024	·009	·045	·012	·036	·010	·023
3000	·014	·038	·011	·059	·015	·047	·017	·028
5000	·016	·064	·020	·103	·021	·070		
8000	·028	·093	·038	·186	·029	·122		
10000	.....	.....	.....	.....	·034	·151		

Summary of Results.

132. The foregoing results may be thus summarized :—

Cells containing zinc and cadmium or cadmium and copper plates, immersed in solutions of the sulphates of these metals respectively, are closely analogous to ordinary Daniell cells (containing zinc sulphate solution). Slight variations in the E.M.F. generated are introduced by varying the condition of the plate-surfaces; but in all cases the maximum E.M.F. actually generated with clean pure plate-surfaces and with solutions of equal molecular strengths is close to that calculable from the net chemical action taking place in the cell when generating a current. When the cadmium plates are not amalgamated, or are covered with crystalline solid amalgam, the electromotive forces are close to ·75 and ·36 volt for cadmium-copper and zinc-cadmium cells respectively, the values corresponding to the net chemical actions as deduced

from Thomsen's thermo-chemical results being substantially the same. When the cadmium plates are covered with fluid amalgam, the electromotive forces are lower in the first case and higher in the second by upwards of ·04 volt—a quantity distinctly exceeding in magnitude the E.M.F. corresponding with the heat of solution of cadmium in mercury, although of the same sign.

(2) The electromotive forces of zinc-silver, cadmium-silver, and copper-silver cells containing the respective sulphates of these metals differ from those of zinc-cadmium, zinc-copper (Daniell), and cadmium-copper cells in this respect, that the maximum electromotive forces generated (the fluids being of equal molecular strength) are not sensibly the same as those calculated from Julius Thomsen's thermal data, but in every case fall short by an amount not far from ·35 volt. When the silver plates are not mercurialized, or are coated with crystalline amalgam, the electromotive forces (which vary slightly with the precise nature of the plate-surfaces) are, in the three cases, near to 1·53, 1·17, and 0·42 volt respectively, the metallic solutions being of equal molecular strength. When the silver plates are covered with fluid amalgam, the electromotive forces are in each case about ·09 volt higher than the values obtained with electro-deposited crystalline metal, this increase almost exactly coinciding with the increment corresponding with the heat of solution of silver in mercury.

(3) As long as the cadmium and zinc [or copper] solutions employed are of the same molecular strength within the limits indicated respectively by $MSO_4\,50H_2O$ and $MSO_4\,1250H_2O$, the E.M.F. developed with a given pair of cadmium and zinc [or copper] plates is sensibly independent of the actual strength of the solutions, these cells behaving precisely like Daniell cells in this respect. With Daniell cells the solutions are practically of the same molecular strength when they are of the same specific gravity; but with the other cells containing cadmium this is not so, cadmium-sulphate solution being uniformly more dense than either zinc or copper solution of the same molecular strength.

(4) The effect on the E.M.F. of a cell of a given alteration in the nature of the surface of either a zinc, copper, cadmium, or silver plate is sensibly the same numerically whichever

other one of these four metals be opposed to it; but the direction of the alteration is opposite according as the plate is the anode or the kathode of the combination.

(5) Volta's "Law of Summation" universally holds within the limits of experimental error in all the cases examined; that is, the electromotive forces of zinc-cadmium, cadmium-copper, and copper-silver combinations are such that, for any given kinds of plate-surfaces, the sums of the two first, of the two last, and of the three together are respectively equal to the electromotive forces of zinc-copper, cadmium-silver, and zinc-silver combinations.

(6) Zinc, copper, and cadmium plates alter superficially (probably in consequence of oxidation by dissolved air) more rapidly when opposed to silver than when opposed to any other one of these four metals, on being immersed in solutions of their respective sulphates forming one half of a cell on Daniell's principle—no current being generated by the cell, the measurements being made by means of a quadrant electrometer.

(7) With all the cells examined the behaviour when generating a current is analogous to that of a normal Daniell cell: when the current-density exceeds a few microampères per square centimetre of plate-surface, a more or less marked diminution in the E.M.F. ensues, the falling-off being the greater the greater the current-density. With moderately strong currents the diminution far exceeds the maximum possible amount due to accumulation of dissolved salt round the plate dissolved, and exhaustion of solution round the other plate. *Cæteris paribus*, the rate of fall in E.M.F. as the current-density increases is the more rapid the lower the heat of formation of the metallic salt decomposed in the cell so as to deposit the metal, and is comparatively but little affected by the nature of the dissolved metal.

(8) The effect of halving the area of the plate on which metal is deposited is usually to cause a greater diminution in the E.M.F. than is produced by halving the area of the dissolved plate; amalgamated cadmium plates in zinc-cadmium cells, however, form an exception to this rule.

XVI. *An Integrating Anemometer.* *By* Walter Baily*.

[Plate VII.]

The object of the instrument described in this paper is to resolve the velocity of the wind in two directions at right angles to one another, and to obtain the time-integral of each part separately.

The instrument contains a horizontal plane, in which are two slits N S and E W, forming a cross to be placed with its arms towards the cardinal points. In these slits are sliders F, G, connected by a bar of constant length. O is the centre of the cross, H the centre of the bar. The locus of H is a circle with centre O. A weathercock or some equivalent mechanism is to keep H in such a position that the radius O H is in the direction of the wind. The sliders carry beneath them wheels, B, C, whose planes are perpendicular to their respective slits, and whose centres are beneath the pivots joining the slits to the bar. [See figs. 1, 2, 3, Plate VII. Fig. 1 gives a perspective view of the instrument, omitting some points; fig. 2 gives a view of the top of the instrument; and fig. 3 gives a section of a slit and slider, and shows the wheel carried by the slider.] The wheels B, C rest on a disk, A (fig. 1), which revolves about a vertical axis immediately below O. The disk A is to be rotated by Robinson's cups, or some equivalent mechanism, so as to have a velocity proportional to that of the wind. The pieces which carry the wheels B, C should be allowed some play in a vertical direction; and the contact of B and C with A can then be maintained either by their own weight or by the use of a spring. The number of rotations of B in a given time is proportional to the time-integral of the resolved part of the wind in one direction (say, north); and the number of rotations of C is proportional to the time-integral of the resolved part of the wind in a direction at right angles to the first (say, west).

Let Ω be the angular velocity of the disk A; ω, ω' the angular velocities of the wheels B, C; m, m' the number of their rotations in a given time t; b their radius, a the length of the bar; θ the angle between the direction of the wind and

* Read June 10, 1882.

(say) the north; then $b\omega = a \sin\theta \,.\, \Omega$, and $b\omega' = a \cos\theta \,.\, \Omega$; and the integrals required are

$$\int_0^t \Omega \sin\theta \, dt = \int_0^t \frac{b}{a} \omega \, dt = \frac{b}{a} \pi m$$

and

$$\int_0^t \Omega \cos\theta \, dt = \int_0^t \frac{b}{a} \omega' dt = \frac{b}{a} \pi m'.$$

Therefore m, m' are proportional to the required integrals.

Each slider might carry a train of wheels to record the number of rotations; or an electrical arrangement might be made in which each wheel should complete a circuit at each rotation and the number of contacts should be recorded. In the latter case, as no distinction is preserved as to the direction in which the wheels revolve, it becomes necessary to have four circuits, one for each cardinal point, with a recorder in each, and to have one connected with each arm of the cross.

A working model of the instrument above described was exhibited at the Meeting, and was fitted with an electrical arrangement such as I have mentioned.

I have since discovered that the slits, sliders, and bar above described may be replaced by a train of cogged wheels. (Fig. 4 represents the upper, and fig. 5 the under surface of the train.) A bar turns in a horizontal plane about O, and is kept in the direction of the wind. This bar carries three wheels, H, K, L, having the same axis. The length of the bar from one pivot to the other is supposed to be an inch and a half. The wheels H, K are rigidly connected; and L lies between them and turns independently. H and K are 1 inch, and L is 3 inches in diameter. L rolls on the inner edge of P, and H rolls on the inner edge of Q, the diameters of P and Q being 6 and 4 inches respectively. Two wheels, M and N, whose diameters are 2 inches, are carried by the wheel L, and have their centres at the extremities of a diameter of L. M and N are in the same plane as K, and are therefore touched by it. As the bar rotates, M and N move without rotation, and their centres move in straight lines passing through O at right angles to one another, and are at a fixed distance apart, and have the line joining them bisected by the bar, which is the direction of the wind. Hence M and N may be used to carry the wheels B, C (fig. 1) instead of their being carried by the sliders F and G.